

# Water Management in Process Plants

---

**David A. Puckett**  
**University of Oklahoma**  
**Department of Chemical, Biological, and Materials Engineering**  
**5/2/2008**

## **Abstract**

One of the primary weaknesses in currently used methods of optimizing water use and reuse in process plants is a lack of accurate modeling of water regeneration operating and capital costs. Both the operating and capital costs of water regeneration processes are generally taken as functions solely of treated water flow rate. However, the results of this assumption do not resemble the observed operating and capital costs trends for many water regeneration processes. The focus of this study was to use physical models of several commonly used water regeneration processes in order to generate general cost curves for these processes suitable for use in water use optimizations. As a result, general curves for process outlet concentration, process equipment cost, and process operating cost for the API separation, activated carbon adsorption, reverse osmosis, and Chevron wastewater treatment processes were generated.

## Executive Summary

In the interests of improving water use optimization model accuracy, physical models of several common processes commonly used in refineries for wastewater regeneration were developed. Specifically, the water regeneration processes modeled were:

- API separation
- Activated carbon adsorption
- Reverse osmosis
- Chevron wastewater treatment

Once physical models for each of these processes were developed, the physical models were used to generate performance data for iterations of each of the processes as the process design variables were altered. Non-linear regression was then used to develop relations between the design variables and the performance of the water regeneration process. Specifically, relations for the following performance aspects were developed.

- Process outlet concentration
- Process equipment cost
- Process operating cost

For each of the processes modeled, the results were as follows:

- API separation
  - $\% \text{ Contaminant Removed} = -35.26e^h + 53.05\ln(L) + \frac{84.82}{1+1.58 \cdot 10^4 e^{-210.31\Delta SG}} + 47.45\ln(D_p) - 120.20\frac{F}{A} - 7.6031$
  - $EC = (\$1.35 \cdot 10^4 F + \$7600\ln(\%QS) - \$1400e^{\Delta SG} - \$1100\ln(D_p) + \$700\ln(h) + \$6700)\frac{PST}{\$833}$
  - $OC = (\$1.14 \cdot 10^5 F)\frac{PE}{\$0.07}$
- Activated carbon adsorption
  - $C_{OUT} = \frac{KC_{IN}^2}{2KC_{IN}+1}$
  - $EC = (\$1100F + \$100C_{IN} + \$2.29 \cdot 10^4 D + \$610H - \$1.26 \cdot 10^4)\left(\frac{0.31 PST}{\$833} + \frac{0.69 PAC}{\$2300}\right)$
  - $OC = (\$8800F + \$2.23 \cdot 10^5 C_{IN})\left(\frac{0.11 PE}{\$0.07} + \frac{0.89 PACR}{\$1840}\right)$
- Reverse osmosis
  - $C_{OUT} = [1 - ((1 - RP)^N)]C_{IN}$
  - $EC = (\$1600F + \$400C_{IN})\left(\frac{PM}{\$90}\right)$
  - $ECs = (\$1600F + \$400C_{IN})\left(\frac{PM}{\$90}\right)[(1 + BR)^{N-1} + 1]$
  - $OC = (\$1100F)\left(\frac{PE}{\$0.07}\right)$
  - $OCs = (\$1100F)\left(\frac{PE}{\$0.07}\right)[(1 + BR)^{N-1} + 1]$

- Chevron wastewater treatment

- $X_{OUT} = -0.0048 \ln(TN) + 0.061 X_{IN} + 0.0011 e^{RBR} - 0.0035 \ln(\eta) + 0.011$
- $X_{OUT} = -0.0049 \ln(TN) + 0.057 X_{IN} + 0.0016 e^{RBR} - 0.011 e^{RFR} - 0.0012 \ln(\eta) + 0.035$
- $EC = (\$14F + \$2900TN + \$2.1 \cdot 10^4 D - \$4000) \frac{PSS}{\$1400}$
- $OC = (\$1.76 \cdot 10^5 F + \$600) \frac{PH}{\$7.33}$

# Table of Contents

Abstract.....	1
Executive Summary.....	2
Introduction .....	5
API Separation.....	7
Activated Carbon Adsorption.....	8
Reverse Osmosis .....	8
Chevron Wastewater Treatment .....	9
Simulation Methods.....	10
API Separation.....	10
Activated Carbon Adsorption.....	12
Reverse Osmosis .....	15
Chevron Wastewater Treatment .....	16
Equipment Cost Estimations .....	17
Operating Cost Estimations .....	19
Results.....	20
Outlet Concentration Curves .....	21
Equipment and Operating Cost Curves.....	27
Recommendations .....	37
Works Cited.....	38
Appendices.....	39
API Separation.....	39
Activated Carbon Adsorption.....	42
Reverse Osmosis .....	46
Chevron Wastewater Treatment .....	50

## Introduction

Many of the process units used in the refining of crude oil treat process water with various contaminants. These contaminants vary from suspended organics to soluble organics, gases, and salts. This contamination forms the primary constraint on the efficient use of process water. It is always more profitable to use the wastewater from one process as the feed water of another process. However, the various process units each have maximum inlet contaminant concentrations at which they will function as designed. Therefore, wastewater regeneration may be necessary before wastewater reuse is possible.

Process	Contaminant	Cin,max (ppm)	Cout,max (ppm)	Mass Load (kg/h)
(1) Caustic Treating	Salts	300	500	0.18
	Organics	50	500	1.2
	H <sub>2</sub> S	5000	11000	0.75
	Ammonia	1500	3000	0.1
(2) Distillation	Salts	10	200	3.61
	Organics	1	4000	100
	H <sub>2</sub> S	0	500	0.25
	Ammonia	0	1000	0.8
(3) Amine Sweetening	Salts	10	1000	0.6
	Organics	1	3500	30
	H <sub>2</sub> S	0	2000	1.5
	Ammonia	0	3500	1
(4) Merox I Sweetening	Salts	100	400	2
	Organics	200	6000	60
	H <sub>2</sub> S	50	2000	0.8
	Ammonia	1000	3500	1
(5) Hydrotreating	Salts	85	350	3.8
	Organics	200	1800	45
	H <sub>2</sub> S	300	6500	1.1
	Ammonia	200	1000	2
(6) Desalter	Salts	1000	9500	120
	Organics	1000	6500	480
	H <sub>2</sub> S	150	450	1.5
	Ammonia	200	400	0

**Table 1: Maximum contaminant loads for refinery processes,(Arnold & Samuel, 2007)**

Various methods of removing contamination from wastewater are used in industry. For the contaminants most commonly encountered in refinery processes, (salts, organics, hydrogen sulfide, and ammonia), some commonly used wastewater treatment processes are as follows.

- Reverse osmosis to remove saline contamination
- API separation and activated carbon adsorption to remove organic contamination
- Chevron wastewater treatment to remove hydrogen sulfide and ammonia

The methods currently used to optimize process water use and regeneration networks make several simplifying assumptions. Primary among these simplifications is the assumption that all costs associated with regeneration are functions solely of the treated wastewater flow rate. It is further assumed that the outlet concentrations of any regeneration process are fixed. However, these assumptions may not be accurate for both operating and capital costs for all wastewater regeneration processes. In particular, it should be noted that two wastewater regeneration systems that process the same amount of wastewater would have the same operating and capital costs regardless of whether one regeneration system was handling very concentrated waste whereas the other system was handling very dilute waste. This trend of constant cost regardless of separation quality is not the trend that would be predicted for most separation processes. Furthermore, consider the situation of two different separation processes, for instance an activated carbon adsorber and a distillation tower, that handle the same flow rate and the same contaminant. Under the simplifying assumptions used in current water use network optimization methods, both the API separator and the distillation tower would have the same operating and capital costs. Obviously this simplifying assumption produces results far from those that would be observed in practice. Therefore, there is a need to develop relations for the outlet concentrations, capital costs, and operating costs for various wastewater regeneration processes in order to remove the

inaccuracies introduced into water use optimization problems through the use of simplifying assumptions.

In this study, several wastewater regeneration processes were analyzed with the intent of developing relations between system design variables and the process outlet concentration, equipment cost, and operating cost. The processes so analyzed were the treatment processes used most often in refineries: API separation, activated carbon adsorption, reverse osmosis, and the Chevron wastewater treatment process. The specifics of each of these treatment options are as follows.

### API Separation

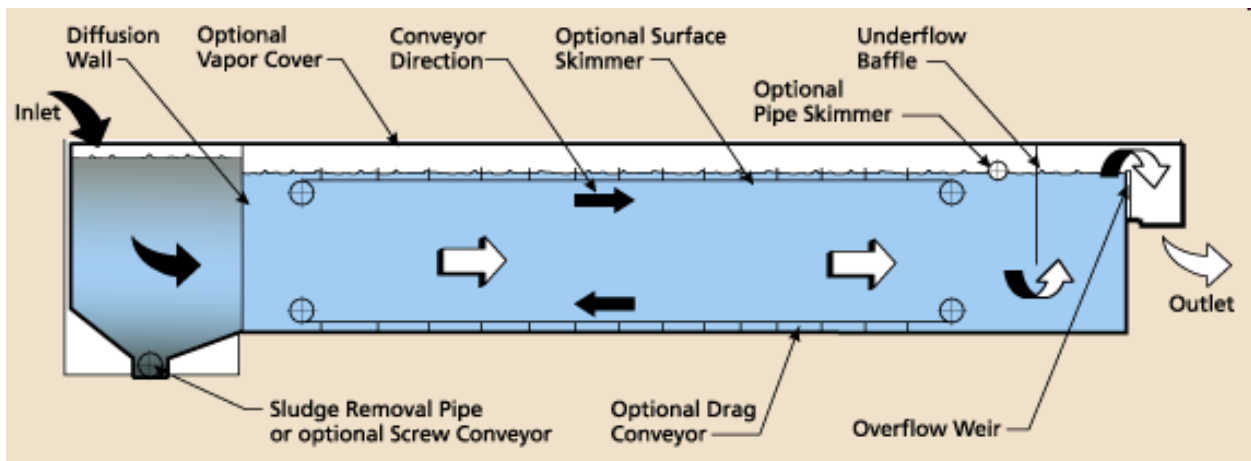


Figure 1: Schematic of an API separator

The API separator works through the specific gravity differences present when water contaminants form a separate phase in water. Contamination will settle to the top or bottom of the separator as it travels through the separator in a stream of wastewater. For a given length and construction of API separator operating at a given flow rate, the quality of separation achieved will be a function solely of the specific gravity and diameter of the contaminant particles. In a refinery, an API separator will be used primarily to remove relatively large diameter (> 150 microns) particles of insoluble organic contaminants.



## Activated Carbon Adsorption

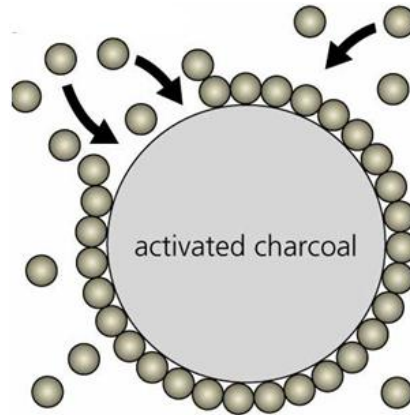


Figure 2: Activated carbon adsorption

The activated carbon adsorber works through a contaminant being more soluble on the surface of an activated carbon particle than in water. Thus, the contaminant will partition favorably in the activated carbon relative to water. For an activated carbon adsorption system that reaches the solubility limit of the activated carbon, the quality of separation achieved will be determined solely by the adsorption thermodynamics, not by the construction of the adsorber. In a refinery, activated carbon adsorption will be used primarily in the removal of soluble and emulsified organics, i.e. organics that cannot be removed via an API separator.

## Reverse Osmosis

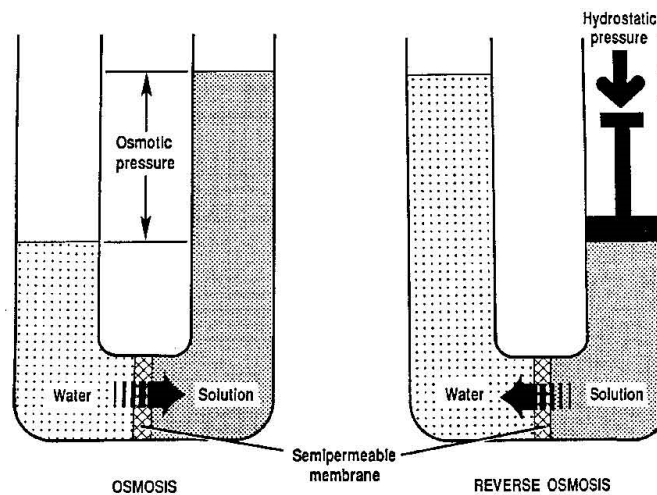
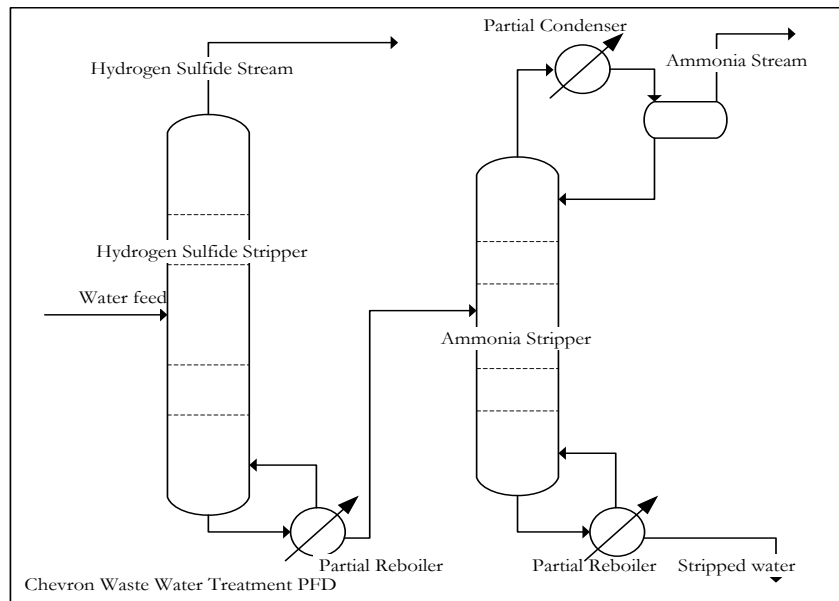


Figure 3: Schematic of a reverse osmosis process

A reverse osmosis separation process works by using external pressure to overcome an osmotic pressure gradient across a membrane selectively permeable to water. For all reverse osmosis systems, the quality of separation achieved is a function solely of the properties of the membrane. Design variables such as membrane thickness and external pressure will only alter the amount of water the reverse osmosis system can process in a given time. In a refinery, reverse osmosis separation process will be used primarily to remove dissolved salts from process water.

### Chevron Wastewater Treatment



**Figure 4: PFD of the Chevron wastewater treatment process**

The Chevron wastewater treatment process consists of stripping column for the removal of hydrogen sulfide in series with a refluxed distillation column for the removal of ammonia. The Chevron wastewater treatment process works through the high volatilities of hydrogen sulfide and ammonia relative to water. By heating a solution of hydrogen sulfide and ammonia in water, a vapor will be produced that will be enriched for hydrogen sulfide and ammonia relative to the original solution. The quality of separation achieved by the Chevron wastewater treatment process is very much dependent on the design variables chosen in the production of the system, especially tray efficiency and tray

number. In a refinery, the Chevron wastewater treatment system will be used solely for the removal of hydrogen sulfide and ammonia from process water although the basic system is suitable for the removal of any contaminant of suitably high volatility.

## Simulation Methods

The method used to develop relations between water regeneration system design variables and the outlet concentrations, equipment costs, and operating costs for the various water regeneration processes is simple in concept but involved in application. Each of the water regeneration processes has one or several fundamental design equations. Using these design equations, the performance and cost of a range of process designs can be modeled. Through non-linear regression, the results of these models can be combined into three fundamental equations; one equation relating outlet concentration to design variables, one equation relating equipment cost to design variables, and one equation relating operating cost to design variables. For each of the water treatment processes modeled, the fundamental design equations used are as follows.

### API Separation

API type separators are used to remove waste water contaminants that are insoluble in water such as sediment, oil, and various insoluble organics. As the contaminants are insoluble, the contaminants will form a separate phase that will settle to either the top or the bottom of the separator based on Stokes Law:

Equation 1

$$V_s = \frac{2 r^2 g \rho_p \rho_f}{9 \mu}$$

Where,  $V_s$  is the settling velocity of the particle,  $r$  is the Stokes radius of the particle,  $g$  is the gravitational acceleration coefficient,  $\rho_p$  is the density of the particle,  $\rho_f$  is the density of the fluid, and  $\mu$  is the viscosity of the fluid the particle is settling through.

As there is flow through the separator while the contaminants are settling, the contaminant particles will have a forward velocity independent of their settling velocity based on the flow rate through the separator. As the API separator specification requires that the separator geometry be such that there is bulk flow through the separator, the horizontal velocity of each contaminant particle should be the bulk velocity of the flow through the separator, (the separator flow rate divided by separator cross sectional area). Using the below equation and Stokes' Law, the minimum particle diameter that will settle can be determined through substitution.

**Equation 2**

$$\frac{H_s}{V_s} = \frac{L_x}{V_x}$$

Where  $H_s$  is the settling distance,  $V_s$  is the settling velocity of the particle as given in equation 1,  $L_x$  is the length of separator, and  $V_x$  is the bulk velocity of flow through the separator.

Any particle larger than the minimum particle size as calculated above will settle in the separator. If a normal distribution is assumed for the contaminant particle diameters and the actual contaminant particle diameter is equal to the Stokes diameter of the particle (i.e. the particles are spherical), the proportion of the contaminant that will settle out in the API separator can be calculated using the following equation:

$$\frac{\int_{r_{\min}}^{\infty} \frac{4}{3} \pi r^3 \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(r-R)^2}{2\sigma^2}} dr}{\int_0^{\infty} \frac{4}{3} \pi r^3 \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(r-R)^2}{2\sigma^2}} dr}$$

Where  $r_{\min}$  is the minimum particle radius that will settle,  $r$  is the particle radius,  $\sigma$  is the standard deviation of the normal particle distribution, and  $R$  is the mean particle radius.

It should be noted that  $\frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(r-R)^2}{2\sigma^2}}$  is the Gaussian probability density function, so the above equation is simply the integral of the volume of any given particle multiplied by the probability of a random particle being of that volume for the particles that settle divided by the same integral for all particles.

### Activated Carbon Adsorption

Removal of a contaminant through adsorption onto activated carbon is modeled by assuming that the limiting factor in mass transfer is pore diffusion, as should be the case with activated carbon of sufficiently high surface area to volume ratio in a non-stagnant fluid. For the pore diffusion limiting case, the following equation should describe the rate of change in contaminant concentration within a spherical activated carbon particle:

$$\frac{\delta C_l}{\delta t} = \frac{\epsilon_p D_{pl}}{\epsilon_p + \rho_p \frac{dN_l}{dC_l}} \frac{\delta}{\delta r} \left[ r^2 \frac{\delta C_l}{\delta r} \right]$$

Where  $C_1$  is the bulk contaminant concentration,  $N_1$  is the amount of contaminant adsorbed onto activated carbon,  $t$  is time,  $r$  is the radial position within the activated carbon particle,  $\varepsilon_p$  is the porosity of the activated carbon particle,  $\rho_p$  is the activated carbon particle density, and  $D_{p1}$  is the diffusivity of the contaminant in the pores of the adsorbent particle (Perry & Green, 1997).

For calculating the amount of contaminant adsorbed at equilibrium, the Langmuir adsorption isotherm was used.

Equation 5

$$N_1 = \frac{N_{IS} K_1 C_1}{1 + K_1 C_1}$$

Where  $N_1$  is the amount of contaminant adsorbed at equilibrium weight of adsorbent,  $N_{IS}$  is the number of adsorbing sites per weight of adsorbent,  $K_1$  is the equilibrium constant for the adsorption, and  $C_1$  is the bulk contaminant concentration.

The solution for the rate of adsorption was found using the linear driving force approximation of the adsorption system adjusted for the pore diffusion limited case as given below:

Equation 6

$$\frac{\partial N_1}{\partial t} = k \left( \frac{N_{IS} \frac{C_1}{C_{IF}}}{R + (R-1) \frac{C_1}{C_{IF}}} - \bar{N}_1 \right)$$

Equation 7

$$k = \frac{15 \Psi (-\varepsilon_p) D_{1p}}{\Lambda r_p^2}$$

Equation 8

$$\Psi = \frac{0.775}{1 - 0.225\sqrt{R}}$$

Equation 9

$$D_{lp} = \frac{D_l}{\tau}$$

Equation 10

$$\varepsilon = \frac{\frac{1}{\rho_b} - \frac{1}{\rho_p}}{\frac{1}{\rho_b}}$$

Equation 11

$$\varepsilon_p = \frac{\frac{1}{\rho_p} - \frac{1}{\rho_s}}{\frac{1}{\rho_p}}$$

Equation 12

$$r_p = \frac{2\varepsilon_p}{A\rho_p}$$

Equation 13

$$\Lambda = \frac{\rho_b N_{IS}}{C_{IF}}$$

Equation 14

$$R = \frac{1}{1 + K_I C_{IF}}$$

Where  $\rho_b$  is bulk density of adsorbent,  $\rho_p$  is particle density of adsorbent,  $\rho_s$  is density of adsorbent skeleton,  $A$  is surface area per weight of adsorbent,  $K_l$  is Langmuir equilibrium coefficient,  $C_l$  is bulk concentration of contaminant,  $C_{IF}$  is feed concentration of contaminant,  $N_l$  is amount of contaminant adsorbed per weight of adsorbent,  $N_{IS}$  is the number of adsorption sites per weight of adsorbent,  $\bar{N}_l$  is the mean amount of contaminant adsorbed in a unit of adsorbent,  $D_l$  is the diffusivity for the contaminant in the working fluid,  $\tau$  is the tortuosity of the adsorbent particle,  $R$  is the separation factor,  $r_p$  is the mean pore diameter for the adsorbent particle,  $\Lambda$  is the partition ratio,  $\epsilon_p$  is the void fraction in the adsorbent particle,  $\epsilon$  is the packing void fraction in the bulk adsorbent,  $D_{ip}$  is the diffusivity for the contaminant in the pores of the adsorbent,  $\Psi$  is the correction factor for pore transfer under the linear driving force assumption,  $k$  is the linear driving force rate constant, and  $t$  is time (Perry & Green, 1997).

### Reverse Osmosis

Removal of salt through reverse osmosis is modeled through a modification of Fick's first law of diffusion to account for diffusion through a semipermeable membrane.

Equation 15

$$N = \frac{P_w}{z} (\Delta P - \Delta \Pi)$$

Where  $N$  is the water flux through the membrane,  $p_w$  is the permeability of the membrane with respect to water,  $z$  is the thickness of the membrane,  $\Delta P$  is the pressure gradient across the membrane, and  $\Delta \Pi$  is the osmotic pressure gradient across the membrane.

The osmotic pressure is determined through the van't Hoff approximation of osmotic pressure:

Equation 16

$$\Pi = cRT$$



Where  $\Pi$  is the osmotic pressure,  $c$  is the total concentration of ions,  $R$  is the gas constant, and  $T$  is the absolute temperature. It should be noted that the van't Hoff approximation is not especially accurate for very concentrated brines. The concentration of ions on the purified water side of the membrane is determined using the rejection ratio for the particular salt that is being removed (a property of the membrane that should be specified by the membrane manufacturer). The amount of rejected salt is similarly calculated from the rejection ratio. If multiple salts are present in significant concentrations, a weighted average rejection ratio can be used. Once the flux through the membrane is determined, the flow rate of water through the reverse osmosis unit can be easily determined through multiplication of the flux and the membrane area.

### **Chevron Wastewater Treatment**

Both the hydrogen sulfide stripper and the ammonia distillation unit in the Chevron wastewater treatment process were simulated using the McCabe-Thiele method taken analytically. An outlet concentration for the waste vapor from both units was assumed in order to provide a starting point for the McCabe-Thiele operating lines. Ideal liquid and vapor mixtures were assumed in obtaining the vapor liquid equilibrium lines. At the reasonably elevated temperatures, and low pressures that the stripping and distillation towers are expected to run at, the system should be close to ideal. For determining the wastewater flow rate through the process, the following relationship to vapor flow rate at flooding was used, with the Souders and Brown factor being approximated from charts in (Peters, Timmerhaus, & West, 2002):

**Equation 17**

$$V_V = C_{SB} \frac{\sigma^{0.2}}{20} \sqrt{\frac{\rho_L - \rho_V}{\rho_V}} \%_F = V_F A = LRA$$

Where  $V_V$  is the vapor velocity in m/s,  $C_{SB}$  is the Souders and Brown factor in m/s,  $\sigma$  is the surface tension of the liquid in dynes/cm,  $\rho_L$  is the liquid density,  $\rho_V$  is the vapor density,  $\%_F$  is the percent of flooding at which the stripping tower or distillation tower is operated,  $V_F$  is the vapor volumetric flow rate,  $A$  is the cross-sectional area of the stripping or distillation tower,  $L$  is the rate of liquid entry into the reboiler, and  $R$  is the fraction of liquid boiled in the reboiler.

### Equipment Cost Estimations

A power law relation between capacity and equipment cost is available for the pricing the pumps necessary for a wastewater regeneration system (Perry & Green, 1997).

Equation 18

$$EC = \$4400 \left( \frac{P}{7.5} \right)^{0.3}$$

Where  $EC$  is the equipment cost for the pump and  $P$  is the power of the pump in kilowatts. The required pump power can be calculated through the following equation (Perry & Green, 1997):

Equation 19

$$P = \frac{HQ\rho}{3.67 \cdot 10^5 \eta}$$

Where  $P$  is the pump power in kilowatts,  $H$  is the dynamic head for the system in meters,  $Q$  is the capacity of the pump in cubic meters per hour,  $\rho$  is the density of the liquid being pumped, and  $\eta$  is the pump efficiency. For all pumps, an efficiency of 75% was assumed for all power calculations.

While power law relations for equipment cost are available for pricing pumps, the same is not true for pricing the main portions of the most of the separation units. Specifically, relations between the equipment costs of API separators, reverse osmosis units, and activated carbon adsorbers had to be developed from whole cloth. For this study, it was assumed that raw materials would form 67% of the

cost of all separators. Furthermore, it was assumed that the casings for all API separators, reverse osmosis units, and activated carbon adsorbers modeled would be composed of 1 cm thick 1020 carbon steel. Based on this thickness, the density of carbon steel, and the measurements of the treatment units modeled, the mass of steel required for each treatment unit can be calculated. The same manner of process can be used for determining the amount of activated carbon initially required for the activated carbon adsorbers. For the reverse osmosis units, it was assumed that cellulose triacetate would be the material used in the construction of the membrane. Membrane specific price was further assumed to be independent of membrane thickness. Based on the quantities of raw materials required, the cost of raw materials was calculated using the following prices.

- Price of 1020 carbon steel: \$833 per ton
- Price of activated carbon: \$2300 per ton
- Price of cellulose triacetate: \$90 per square meter

It should be noted that these prices were only used in obtaining the initial data used in developing equipment cost relations. The equipment cost relations themselves provide an adjustment factor for the actual price of the raw materials in question.

The equipment costs for the stripping and distillation columns required for the Chevron wastewater treatment process were priced by fitting lines to charts provided in (Peters, Timmerhaus, & West, 2002). Briefly stated, the equipment cost for a stripping or distillation column is taken to be a factor of column diameter and the number of trays present in the column as well as the material used in the construction of the column. For the purposes of this study, it was assumed that all columns would be constructed completely out of stainless steel. As the Chevron wastewater treatment process is used for the removal of corrosive gas components from water, it is reasonable to assume that stainless steel would be used in the construction of the requisite columns in order to reduce the risk of corrosion.

While a price for stainless steel was not required to use the charts in (Peters, Timmerhaus, & and West, 2002), a price for stainless steel at the time the charts were generated is be necessary for adjusting the results obtained from the charts to current stainless steel prices. For the purpose of adjustment, the following price for stainless steel in 2002 was used.

- Price of stainless steel: \$1400 per ton

### **Operating Cost Estimations**

For all of the water treatment processes modeled, a significant operating cost for the process is the cost of pumping the water to be treated through the treatment process. For an API separator or a reverse osmosis unit, the cost of pumping amounts to the primary operating cost. For the refluxed distillation tower used in the Chevron wastewater treatment process, additional pumping costs come from the requirement for cooling water in the column condenser. As the pumping power required for each system has already been calculated for the sizing of the pump required for the system, the operating cost for pumping is found through the application of the price of electrical power. For the purposes of this study, a price of \$0.07 per kilowatt-hour was assumed for all operating cost calculations. However, in a similar fashion to the raw materials prices, a factor was provided in all obtained operating cost relations to adjust the operating cost to the current price of electricity.

For the activated carbon adsorbers, an additional operating cost above the cost of pumping water through the system consists of regenerating the activated carbon used in the adsorption. The cost of regenerating the activated carbon was assumed to be 65% of the cost of obtaining virgin activated carbon with an additional 15% of the cost of obtaining virgin activated carbon added on to represent the losses of activated carbon in the regeneration process. These assumptions regarding the cost of regenerating the activated carbon would be reasonably accurate if the activated carbon used in the adsorber were regenerated off-site. If regeneration were performed on-site, savings may be

possible if significant enough quantities of activated carbon were being regenerated. Similarly to all of the other costs associated with the regeneration processes, a correction factor was provided to account for activated carbon regeneration cost savings.

For the stripping and distillation columns used in the Chevron wastewater treatment process, reboiler heat duty presented an additional operating cost above pumping requirements. For both of the column types, reboiler duty was calculated using the reboil ratio for the partial reboiler (the fraction of the liquid entering the reboiler that is boiled) and the heat capacity and heat of vaporization of water. For the likely percentage of hydrogen sulfide and ammonia present in the water being treated in the Chevron wastewater treatment process, the contribution of hydrogen sulfide and ammonia to the heat capacity and heat of vaporization of the wastewater was assumed to be negligible. Similarly, the effect of mixture non-idealities on the heat duty of the reboiler was also assumed to be of negligible importance. For providing the heat to the reboiler, it was assumed that the fundamental source of the heat would be combustion of natural gas with 85% of the lower heating value of the gas being available for heating the column. A price of \$7.33 per MMBTU was assumed the cost of natural gas. Similarly to all of the other costs, a correction factor for differing prices of heat was provided.

## **Results**

Using the modeling equations and assumptions stated previously, the outlet concentrations, equipment costs, and operating costs for the four water treatment processes analyzed were obtained with varying design parameters. Non-linear regression was used to fit multivariable curves to the data so generated.

## Outlet Concentration Curves

For all of the water treatment methods analyzed in this study, the outlet concentration of the treatment process can be calculated directly from the design equations for the process. However, for several water treatment methods, specifically API separation and the Chevron wastewater treatment method, the exact calculation method is cumbersome to use in water use optimizations. To simplify the implementation of the outlet concentration curves in water use optimizations, it is possible to express the exact solutions for outlet concentration as a combination of non-linear functions through the use of regression. The regression option was chosen for use with the outlet concentrations of the API separation process, where outlet concentration is determined through an integral that can only be evaluated numerically, and the Chevron wastewater treatment process, where outlet concentration is the product of a system of equations, in order to simplify equation implementation.

### *API Separation*

The outlet concentration of an API separator can be calculated exactly, if a normal distribution of particle diameters is assumed and the particles are uniformly spherical, through the application of Stokes' Law and the following solution to equation 3.

Equation 20

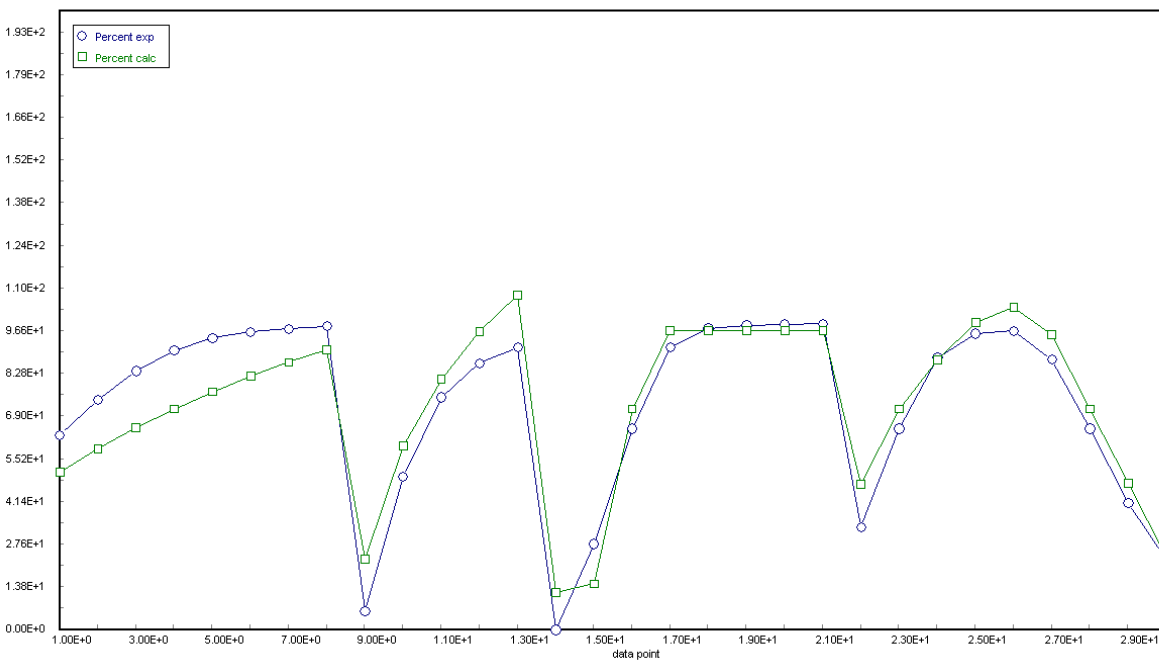
*% Contaminant Removed*

$$= \frac{e^{\frac{-r_{min}^2 + 2r_{min}R}{2\sigma^2}} \left( -2\sigma(r_{min}^2 + r_{min}R + R^2 + 2\sigma^2) + e^{\frac{r_{min}^2 - 2r_{min}R + R^2}{2\sigma^2}} \sqrt{2\pi}R(R^2 + 3\sigma^2) \operatorname{Erf} \left( \frac{r_{min} - R}{\sqrt{2}\sigma} \right) \right)}{\left( -2\sigma(R^2 + 2\sigma^2) + e^{\frac{R^2}{2\sigma^2}} \sqrt{2\pi}R(R^2 + 3\sigma^2) \operatorname{Erf} \left( \frac{R}{\sqrt{2}\sigma} \right) \right)}$$

Equation 21

$$C_{OUT} = \% \text{ Contaminant Removed } C_{IN}$$

Where  $r_{\min}$  is the minimum radius of particle that will settle in the API separator as given by Stokes' Law,  $R$  is the mean particle radius,  $\sigma$  is the standard deviation in the particle size distribution,  $C_{OUT}$  is the outlet concentration to the separator, and  $C_{IN}$  is the inlet concentration to the separator. In the interests of easy implementation of this simulation of the API separator in a water use optimization, the following regression for the dependence of the outlet concentration of an API separator on the design parameters of the separator was performed.



**Figure 5: Non-linear regression for API separator outlet concentration**

It should be noted that since this is a multivariable regression, the axis of abscissas cannot reference any particular variable. Thus, the axis of abscissas is simply marked off with the number of the data point used in the regression whereas the axis of ordinates references the objective function achieved at the combination of variables the data point references (in the case of an API separator, the percentage of contaminants removed). The various peaks in the graph were generated by a single variable being varied while all other variables were held constant. Through data point 8, settling

distance was varied. From data point 9 to data point 13, separator length was varied. From data point 14 to data point 21, the difference in specific gravity between the contaminant and water was varied. From data point 22 to data point 26, contaminant mean particle diameter was varied. From data point 27 on, the wastewater velocity was varied. For the graphs, blue markers represent the simulation results whereas green markers represent the results of the regression. From this regression, the following relation between the design variables for the API separator and the percentage of contamination removed was developed.

**Equation 22**

*% Contaminant Removed*

$$= -35.26e^h + 53.05\ln(L) + \frac{84.82}{1 + 1.58 \cdot 10^4 e^{-210.31\Delta SG}} + 47.45\ln(D_p) - 120.20 \frac{F}{A} - 7.6031$$

Where h is the settling distance in meters, L is the separator length in meters,  $\Delta SG$  is the difference in specific gravity between the contaminant and water,  $D_p$  is the mean contaminant particle diameter in millimeters, F is the volumetric flow rate through the separator in cubic meters per second, and A is the cross sectional area of the separator in square meters. Equation 21 can then be used to take the percentage of contamination removed and generate the outlet concentration. As figure 5 indicates, the regression should prove reasonably accurate for variations in most of the design variables for the API separator. However, a more transcendental dependence of the percentage of contamination removed on settling distance may result in a better fit overall.

### ***Activated Carbon Adsorption***

The outlet concentration of an activated carbon adsorber can be calculated easily and simply from the Langmuir adsorption isotherm if the adsorber reaches equilibrium with the feed to the adsorber.



$$C_{OUT} = \frac{KC_{IN}^2}{2KC_{IN} + 1}$$

Where K is the Langmuir adsorption coefficient,  $C_{OUT}$  is the outlet concentration of the adsorber, and  $C_{IN}$  is the inlet concentration of the adsorber.

### ***Reverse Osmosis***

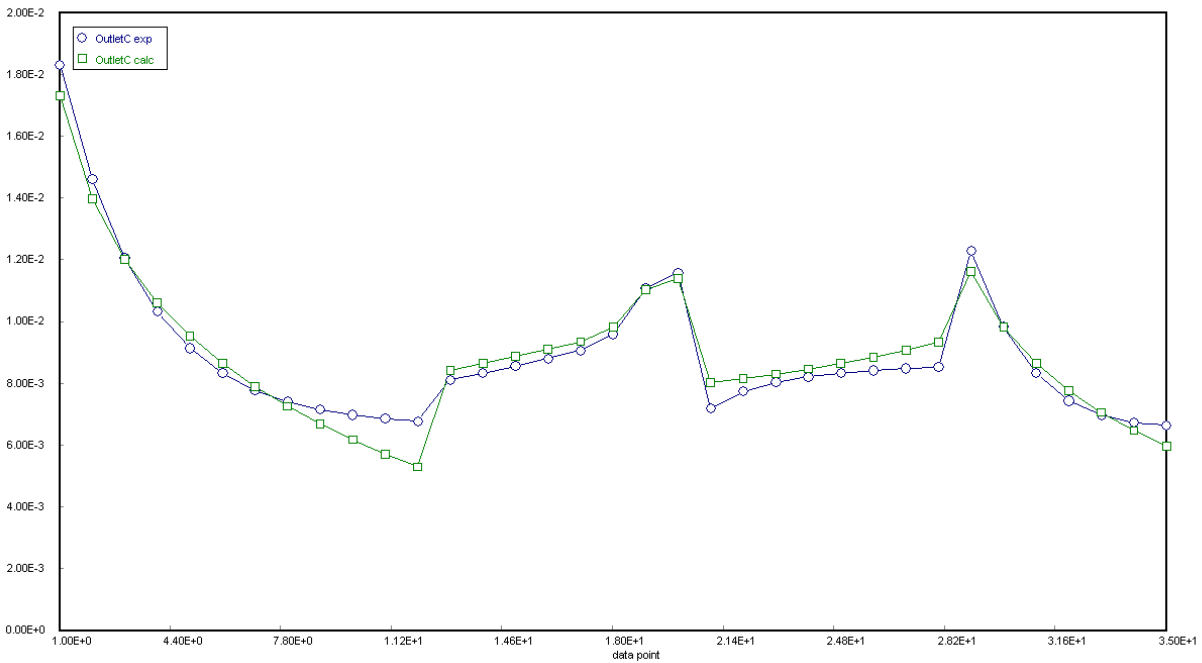
The outlet concentration of a reverse osmosis unit can be calculated easily and simply from the design parameters of the unit as follows.

$$C_{OUT} = [1 - ((1 - RP)^N)]C_{IN}$$

Where RP is the rejection percentage of the membrane for the contaminant in question, N is the number of membranes connected in series,  $C_{OUT}$  is the outlet concentration of the reverse osmosis unit, and  $C_{IN}$  is the inlet concentration of the reverse osmosis unit.

### ***Chevron Wastewater Treatment***

Similarly to the case of the API separator, regressions were used to develop general relations between outlet concentration and the design variables for the columns used in the Chevron wastewater treatment process. The curve obtained for the hydrogen sulfide stripping column is as follows.



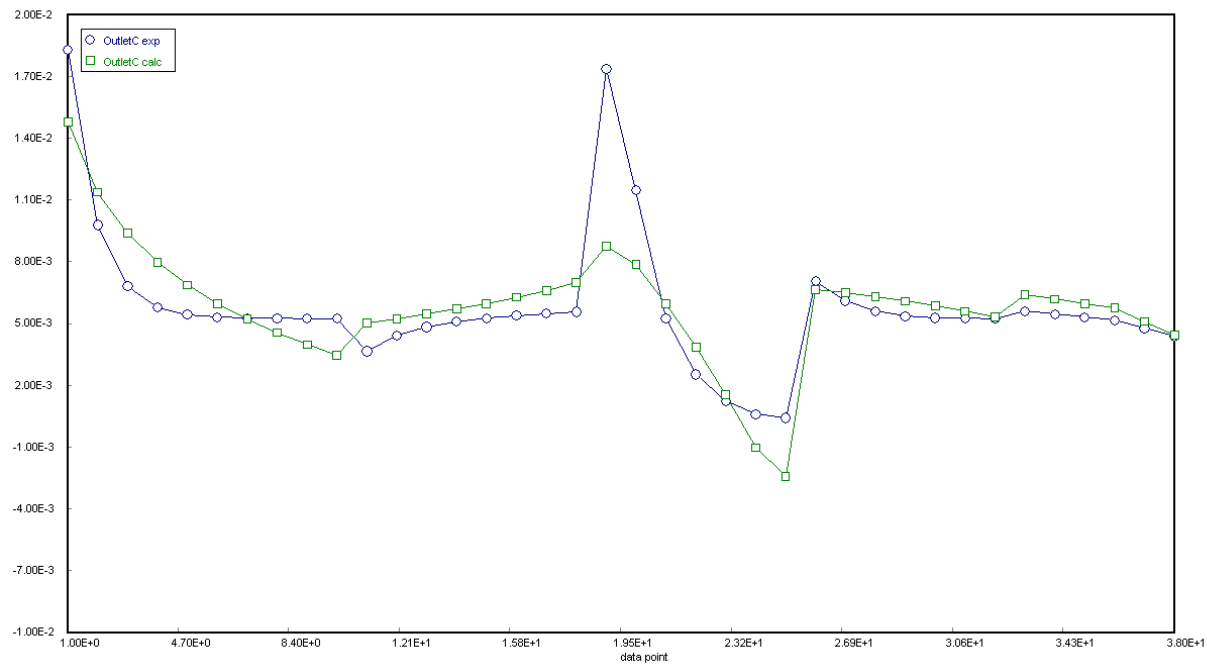
**Figure 6: Non-linear regression for hydrogen sulfide stripping column outlet concentration**

It should be noted that since this is a multivariable regression, the axis of abscissas cannot reference any particular variable. Thus, the axis of abscissas is simply marked off with the number of the data point used in the regression whereas the axis of ordinates references the objective function achieved at the combination of variables the data point references (in the case of a hydrogen sulfide stripper, the outlet mole fraction of contamination). The various peaks in the graph were generated by a single variable being varied while all other variables were held constant. Through data point 12, tray number was varied. From data point 13 to data point 20, inlet mole fraction of contaminant was varied. From data point 21 to data point 28, the reboil ratio was varied. From data point 29 on, mean tray efficiency was varied. For the graphs, blue markers represent the simulation results whereas green markers represent the results of the regression. From this regression, the following relation between the design variables for the hydrogen sulfide stripper and the outlet mole fraction of contamination was developed.

$$X_{OUT} = -0.0048 \ln(TN) + 0.061 X_{IN} + 0.0011 e^{RBR} - 0.0035 \ln(\eta) + 0.011$$

Where TN is the number of trays in the column, RBR is the reboil ratio,  $\eta$  is the mean tray efficiency,  $X_{OUT}$  is the mole fraction of contaminant at the outlet of the column, and  $X_{IN}$  is the mole fraction of contaminant at the inlet to the column.

A similar regression can be performed for the refluxed distillation column used for ammonia removal.



**Figure 7: Non-linear regression for ammonia distillation column outlet concentration**

It should be noted that since this is a multivariable regression, the axis of abscissas cannot reference any particular variable. Thus, the axis of abscissas is simply marked off with the number of the data point used in the regression whereas the axis of ordinates references the objective function achieved at the combination of variables the data point references (in the case of a ammonia distillation column, the outlet mole fraction of contamination). The various peaks in the graph were generated by a

single variable being varied while all other variables were held constant. Through data point 10, tray number was varied. From data point 11 to data point 18, inlet mole fraction of contaminant was varied. From data point 19 to data point 25, the reflux ratio was varied. From data point 26 to data point 32, reboil ratio was varied. From data point 33 on, mean tray efficiency was varied. For the graphs, blue markers represent the simulation results whereas green markers represent the results of the regression. From this regression, the following relation between the design variables for the hydrogen sulfide stripper and the outlet mole fraction of contamination was developed.

**Equation 26**

$$X_{OUT} = -0.0049\ln(TN) + 0.057X_{IN} + 0.0016e^{RBR} - 0.011e^{RFR} - 0.0012\ln(\eta) + 0.035$$

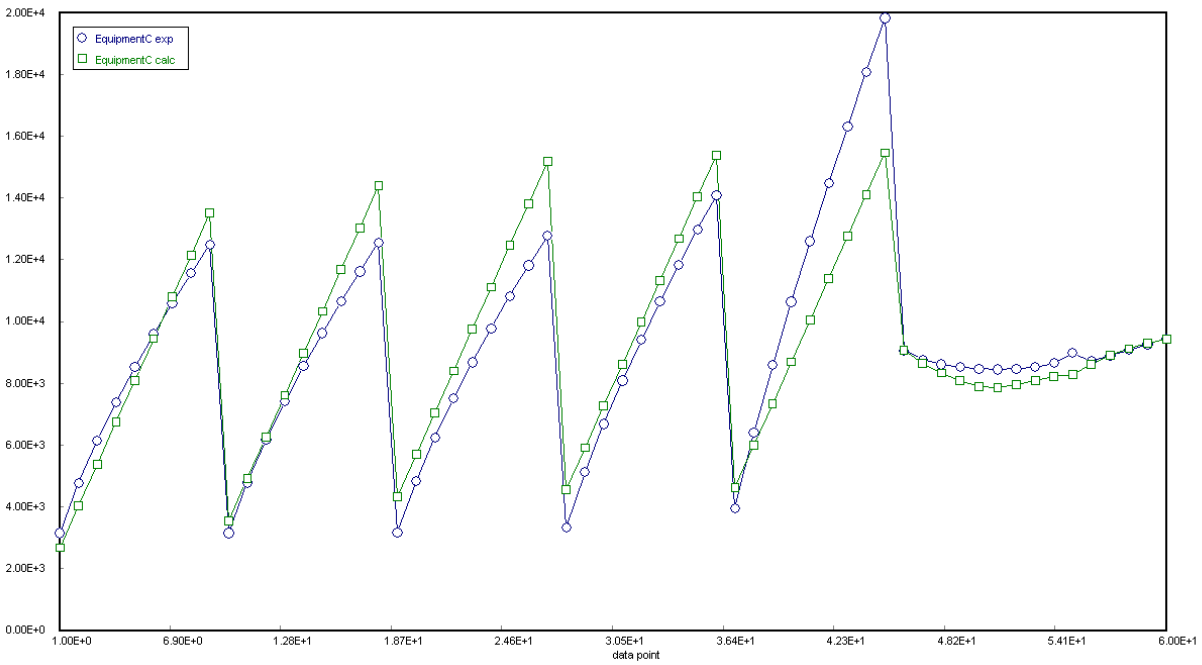
Where TN is the number of trays in the column, RBR is the reboil ratio, RFR is the reflux ratio,  $\eta$  is the mean tray efficiency,  $X_{OUT}$  is the mole fraction of contaminant at the outlet of the column, and  $X_{IN}$  is the mole fraction of contaminant at the inlet to the column. It should be noted that the regression does show some deviation from the predicted data at low reflux ratios close to the minimum reflux ratio for the column due to the requirement for an infinite column height at minimum reflux.

### **Equipment and Operating Cost Curves**

For all of the water treatment methods analyzed in this study, relations for equipment cost and operating cost were obtained as combinations of transcendental functions through non-linear regression. Exact solutions for the equipment cost and operating cost of each of the water treatment methods analyzed are possible, but the use of regression was chosen for ease of implementation. If fixed capital investment relations are required instead of equipment cost relations, the equipment cost curves obtained for each of the water treatment methods can be multiplied by a constant Lang factor.

### ***API Separation***

The following regression was performed for the equipment cost for an API separator.



**Figure 8: Non-linear regression for the equipment cost for an API separator**

It should be noted that since this is a multivariable regression, the axis of abscissas cannot reference any particular variable. Thus, the axis of abscissas is simply marked off with the number of the data point used in the regression whereas the axis of ordinates references the equipment cost achieved at the combination of variables the data point. The various peaks in the graph were generated by a single variable being varied while all other variables were held constant. Through data point 45, the quality of separation achieved in the API separator was varied in steps over a range of flow rates. From data point 46 to data point 51, the difference in specific gravity between the contaminant and water was varied. From data point 52 to data point 56, the mean contaminant particle diameter was varied. From data point 57 on, the settling height for the separator was varied. For the graphs, blue markers represent the simulation results whereas green markers represent the results of the regression. From the same variables, the following regression for the operating cost of an API separator was performed.

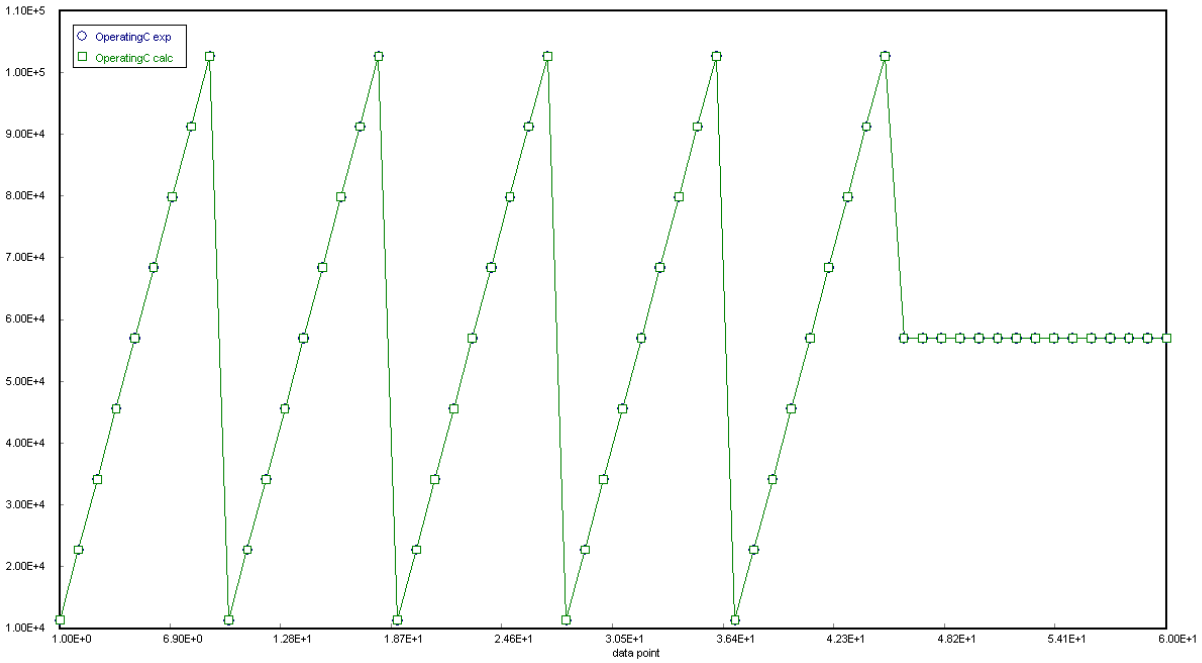


Figure 9: Non-linear regression for the operating cost for an API separator

From these regressions, the following relations between the design variables for the API separator and the equipment cost and operating cost of the separator were developed.

Equation 27

$$EC = (\$1.35 \cdot 10^4 F + \$7600 \ln(\%QS) - \$1400 e^{\Delta SG} - \$1100 \ln(D_p) + \$700 \ln(h) + \$6700) \frac{PST}{\$833}$$

Equation 28

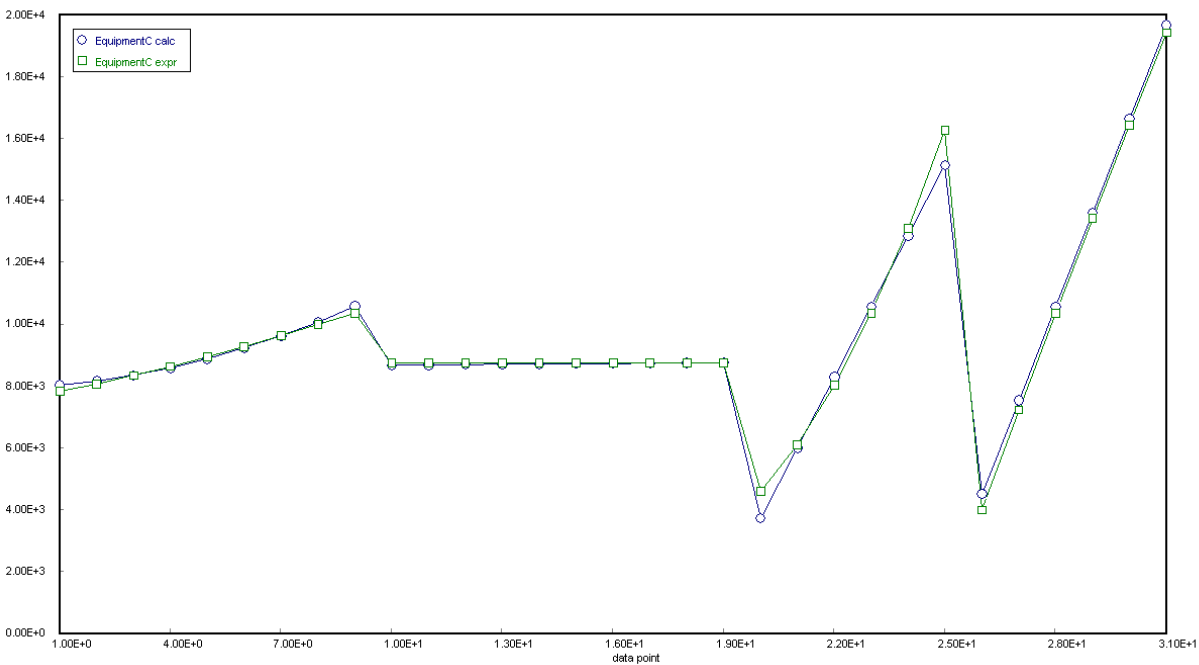
$$OC = (\$1.14 \cdot 10^5 F) \frac{PE}{\$0.07}$$

Where F is the flow rate through the system in cubic meters per second, %QS is the percentage of contaminant removed,  $\Delta SG$  is the difference in specific gravity between the contaminant and water,  $D_p$  is the mean contaminant particle diameter in millimeters, h is the settling height for the separator in meters, PST is the current price of steel in dollars per ton, PE is the current price of electricity in dollars

per kilowatt-hour, EC is the equipment cost for the separator, and OC is the operating cost of the separator. It should be noted that the regression for equipment cost breaks from the simulated results for separation qualities above 99.5% due to the length of the separator approaching infinity as the quality of separation approaches 100%.

### **Activated Carbon Adsorption**

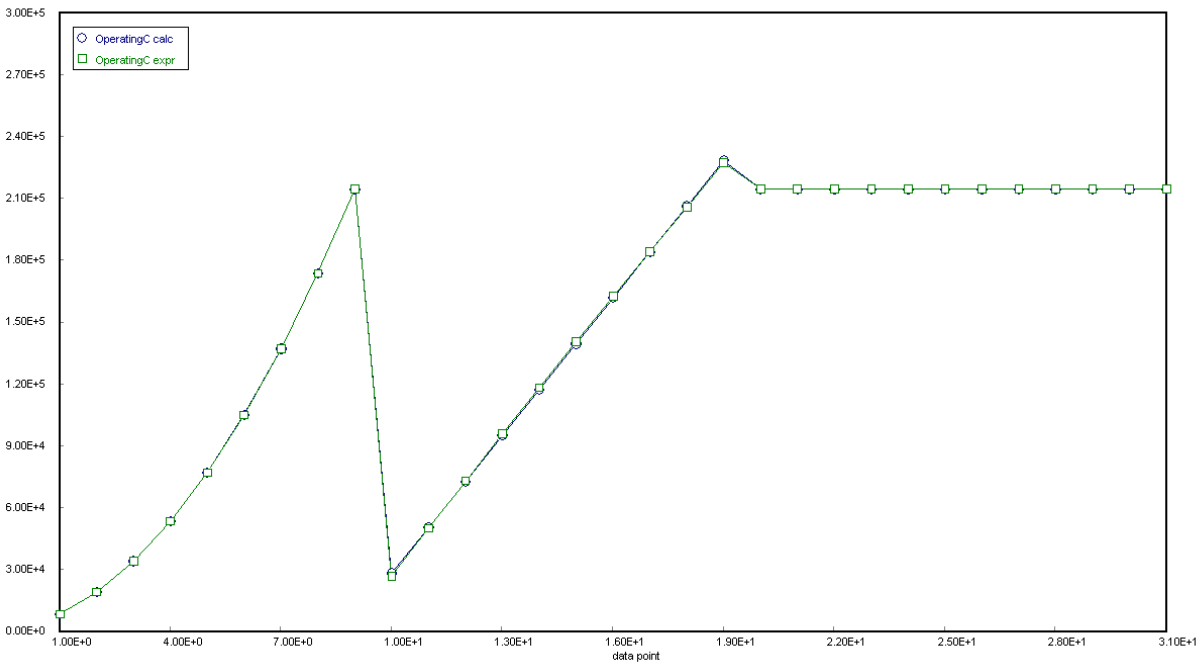
The following regression was performed for the equipment cost for an activated carbon adsorber.



**Figure 10: Non-linear regression for the equipment cost for an activated carbon adsorber**

It should be noted that since this is a multivariable regression, the axis of abscissas cannot reference any particular variable. Thus, the axis of abscissas is simply marked off with the number of the data point used in the regression whereas the axis of ordinates references the equipment cost achieved at the combination of variables the data point. The various peaks in the graph were generated by a single variable being varied while all other variables were held constant. Through data point 9, the

flow rate through the adsorber was varied. From data point 10 to data point 19, the contaminant concentration at the inlet to the adsorber was varied. From data point 20 to data point 25, the height of the adsorber was varied. From data point 26 on, the diameter of the adsorber was varied. For the graphs, blue markers represent the simulation results whereas green markers represent the results of the regression. From the same variables, the following regression for the operating cost of an activated carbon adsorber was performed.



**Figure 11: Non-linear regression for the operating cost for an activated carbon adsorber**

From these regressions, the following relations between the design variables for the activated carbon adsorber and the equipment cost and operating cost of the adsorber were developed.

**Equation 29**

$$EC = (\$110F + \$100C_{IN} + \$2.29 \cdot 10^4 D + \$610H - \$1.26 \cdot 10^4) \left( \frac{0.31 PST}{\$833} + \frac{0.69 PAC}{\$2300} \right)$$



$$OC = (\$8800F + \$2.23 \cdot 10^5 C_{IN}) \left( \frac{0.11 PE}{\$0.07} + \frac{0.89 PACR}{\$1840} \right)$$

Where F is the flow rate through the system in cubic meters per hour,  $C_{IN}$  is contaminant concentration at the inlet to the adsorber in kilograms per cubic meter, D is the diameter of the adsorber in meters, H is the height of the adsorber in meters, PST is the current price of steel in dollars per ton, PAC is the current price of activated carbon in dollars per ton, PE is the current price of electricity in dollars per kilowatt-hour, PACR is the current price of activate carbon regeneration in dollars per ton, EC is the equipment cost for the adsorber, and OC is the operating cost of the adsorber.

### Reverse Osmosis

The following regression was performed for the equipment cost of a reverse osmosis unit.

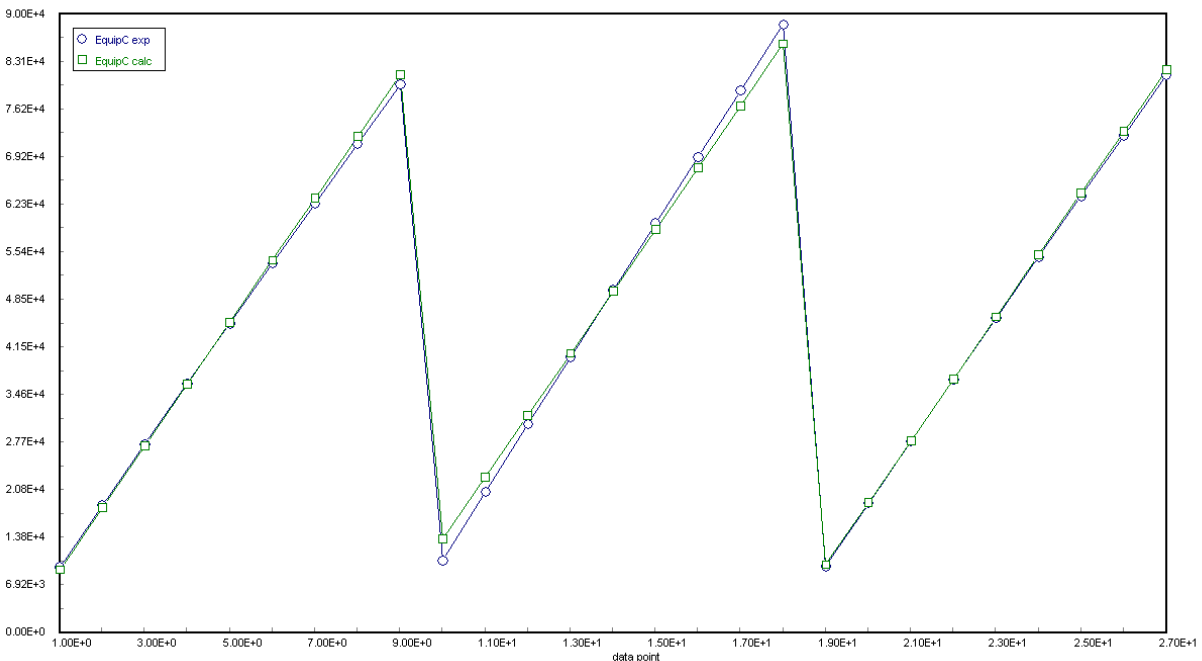
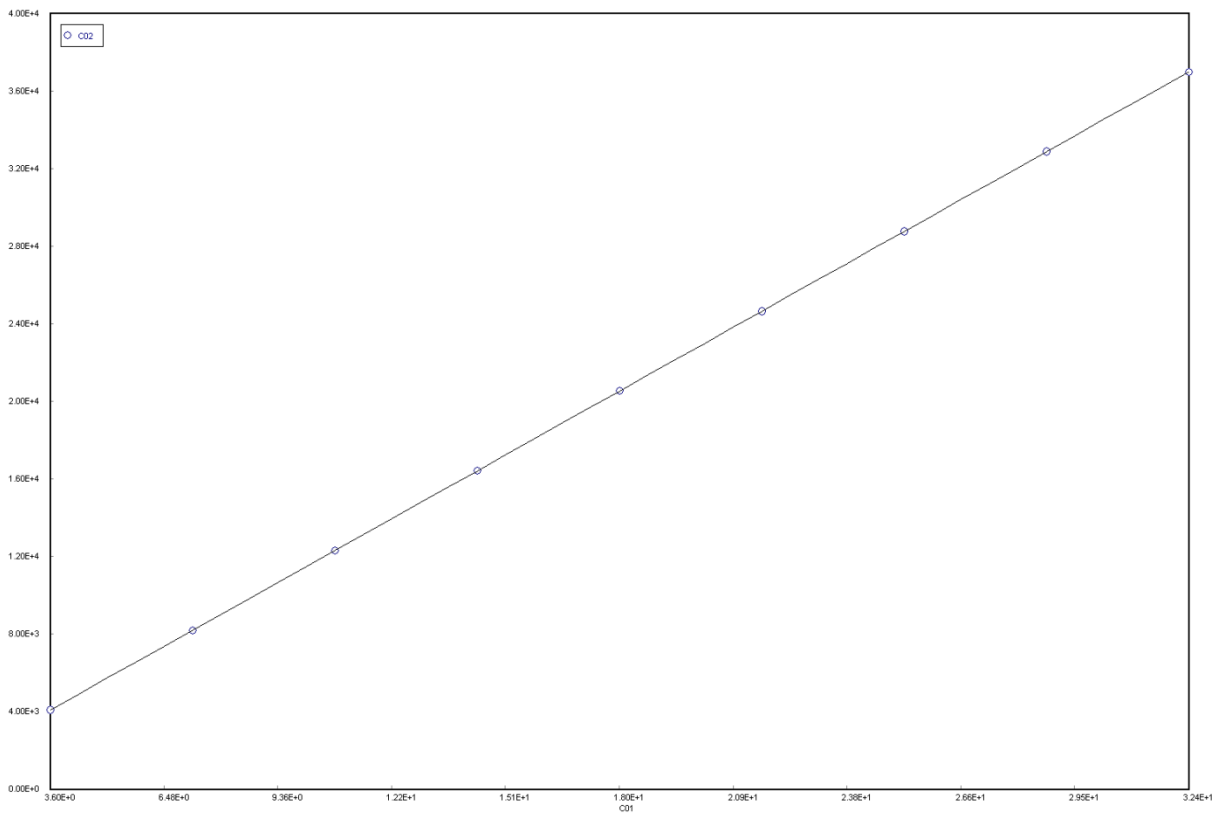


Figure 12: Non-linear regression for the equipment cost for a reverse osmosis unit

It should be noted that since this is a multivariable regression, the axis of abscissas cannot reference any particular variable. Thus, the axis of abscissas is simply marked off with the number of the data point used in the regression whereas the axis of ordinates references the equipment cost achieved at the combination of variables the data point. The various peaks in the graph were generated by a single variable being varied while all other variables were held constant. For the whole of the data set used in the regression, the inlet concentration to the reverse osmosis unit was varied in steps over a range of flow rates. For the graphs, blue markers represent the simulation results whereas green markers represent the results of the regression. From the same variables, the following regression for the operating cost of a reverse osmosis unit was performed.



**Figure 13: Linear regression for the operating cost for a reverse osmosis unit**

From these regressions, the following relations between the design variables for the reverse osmosis unit and the equipment cost and operating cost of the unit were developed for single membranes and for membranes in series.

**Equation 31**

$$EC = (\$1600F + \$400C_{IN}) \left( \frac{PM}{\$90} \right)$$

**Equation 32**

$$ECs = (\$1600F + \$400C_{IN}) \left( \frac{PM}{\$90} \right) [(1 + BR)^{N-1} + 1]$$

**Equation 33**

$$OC = (\$1100F) \left( \frac{PE}{\$0.07} \right)$$

**Equation 34**

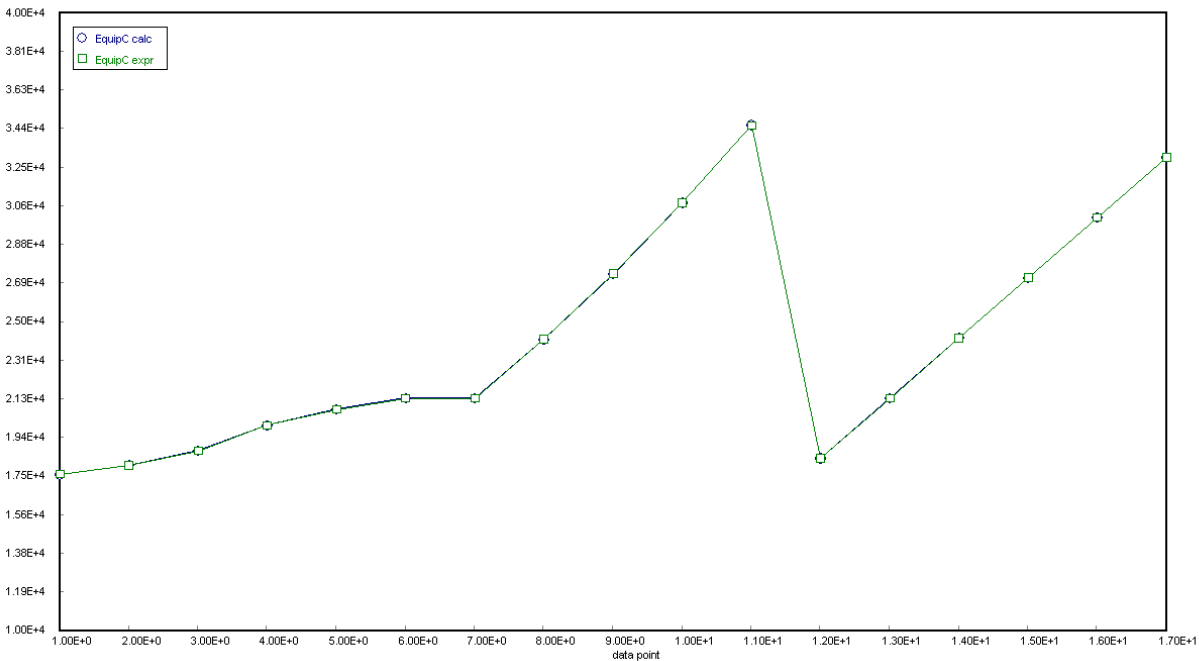
$$OCs = (\$1100F) \left( \frac{PE}{\$0.07} \right) [(1 + BR)^{N-1} + 1]$$

Where F is the flow rate through the system in cubic meters per hour,  $C_{IN}$  is contaminant concentration at the inlet to the adsorber in moles per cubic meter, BR is the bypass ratio for the membrane (the fraction of water that enters the inlet of the membrane unit that is retained), N is the number of membranes in series, PM is the current price of the membrane in dollars per square meter, PE is the current price of electricity in dollars per kilowatt-hour, EC is the equipment cost for the reverse osmosis unit for the case of a single membrane, ECs is the equipment cost for the reverse osmosis unit for the case of membranes in series, OC is the operating cost of the reverse osmosis unit for the case of a single

membrane, and OCs is the operating cost of the reverse osmosis unit for the case of membranes in series.

### ***Chevron Wastewater Treatment***

The equipment and operating costs for the stripping and distillation columns used in the Chevron wastewater treatment process both follow the same trends in equipment and operating cost. Thus, it is only necessary to perform regressions for equipment and operating cost for either the stripping column or the distillation column in order to develop relations that are appropriate for both types of column. The following regression was performed for the equipment cost of a stripping or distillation column.



**Figure 14: Non-linear regression for the equipment cost for a stripping or distillation column**

It should be noted that since this is a multivariable regression, the axis of abscissas cannot reference any particular variable. Thus, the axis of abscissas is simply marked off with the number of the data point used in the regression whereas the axis of ordinates references the equipment cost

achieved at the combination of variables the data point. The various peaks in the graph were generated by a single variable being varied while all other variables were held constant. Through data point 7, the flow rate through the column was varied. From data point 8 to data point 11, the number of trays in the column was varied. From data point 12 on, the diameter of the column was varied. For the graphs, blue markers represent the simulation results whereas green markers represent the results of the regression. From the same variables, the following regression for the operating cost of a stripping or distillation column was performed.

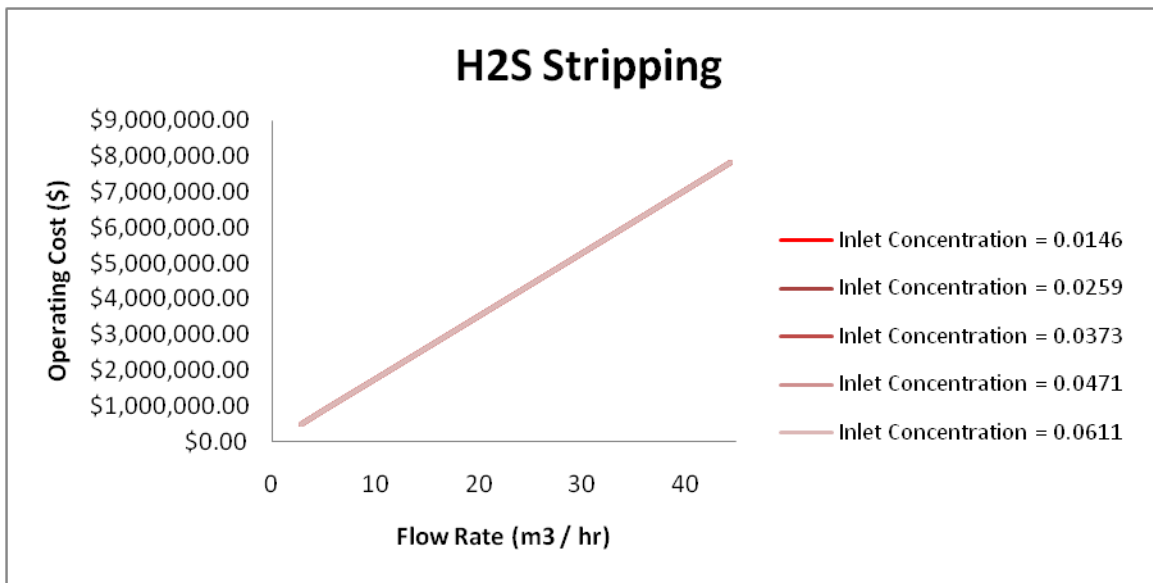


Figure 15: Linear regression for the operating cost for a stripping or distillation column

From these regressions, the following relations between the design variables for a stripping or distillation column and the equipment cost and operating cost of the column were developed.

Equation 35

$$EC = (\$14F + \$2900TN + \$2.1 \cdot 10^4 D - \$4000) \frac{PSS}{\$1400}$$

$$OC = (\$1.76 \cdot 10^5 F + \$600) \frac{PH}{\$7.33}$$

Where F is the flow rate through the system in cubic meters per hour, TN is the number of trays in the column, D is the diameter of the column in meters, PSS is the current price of stainless steel in dollars per ton, PH is the current price of heat in dollars per MMBTU, EC is the equipment cost for the column, and OC is the operating cost of the column.

## Recommendations

In order to develop water use optimization methods of greater accuracy than the methods currently used, a reduction in the use of simplifying assumptions is necessary. Specifically, the assumptions of fixed regeneration process outlet concentration and flow rate dependent costs introduce inaccuracies into water use optimization models. Through the direct substitution of the relations for process outlet concentration, process equipment cost, and process operating cost developed in this study for the assumed outlet concentrations and costs, these modeling inaccuracies can be rectified for some of the more common water regeneration methods. For water regeneration processes not covered in this study, a similar method of rectifying modeling inaccuracies as used in this study can be applied (i.e. a physical model of the process can be developed, the physical model can be used to generate performance data for a variety of process designs, and non-linear regressions can be performed on this data to develop relations for process outlet concentration, equipment cost, and operating cost). Similarly, water contaminating processes could be modeled in the same manner to remove further sources of inaccuracy in water use optimization models.

## Works Cited

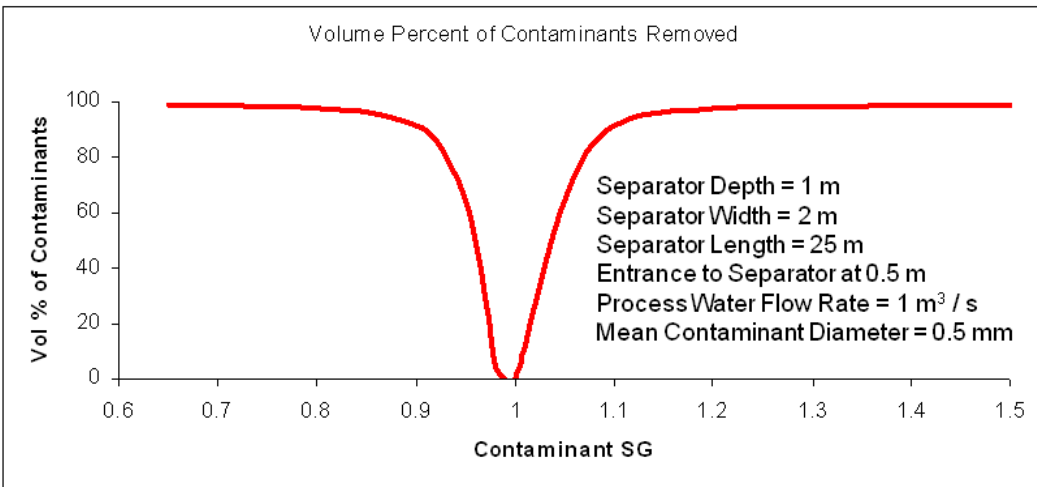
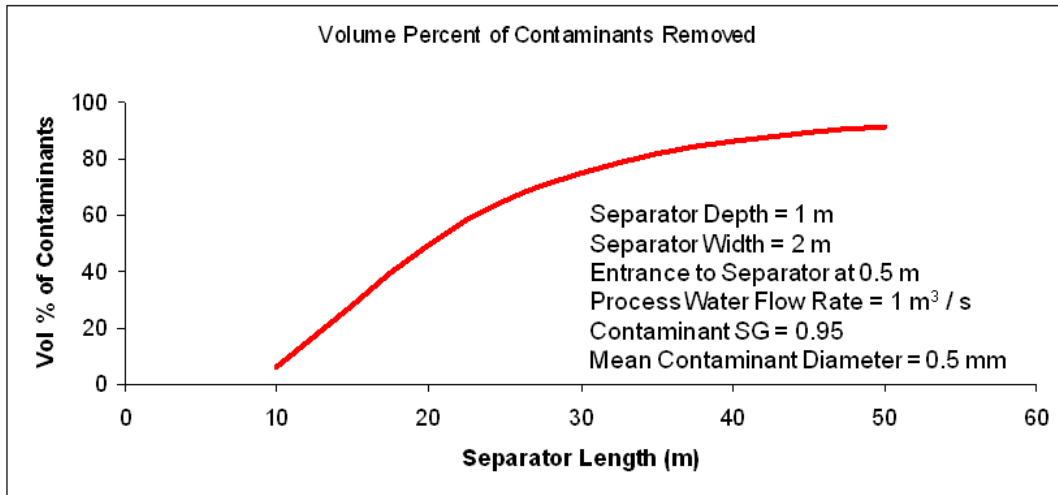
Arnold, M. C., & Samuel, J. (2007). *Water Management in Refineries*.

Perry, R., & Green, D. (1997). *Perry's Chemical Engineers' Handbook* (7th ed.). McGraw-Hill.

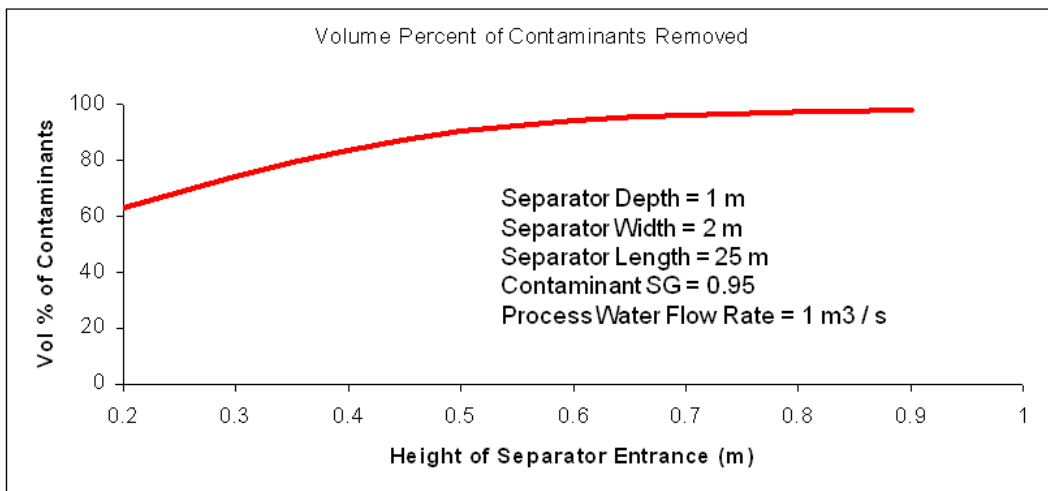
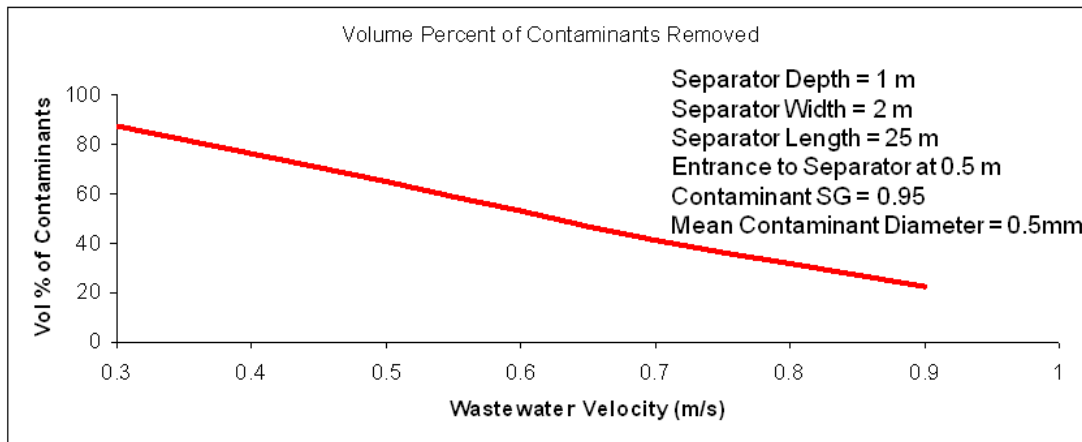
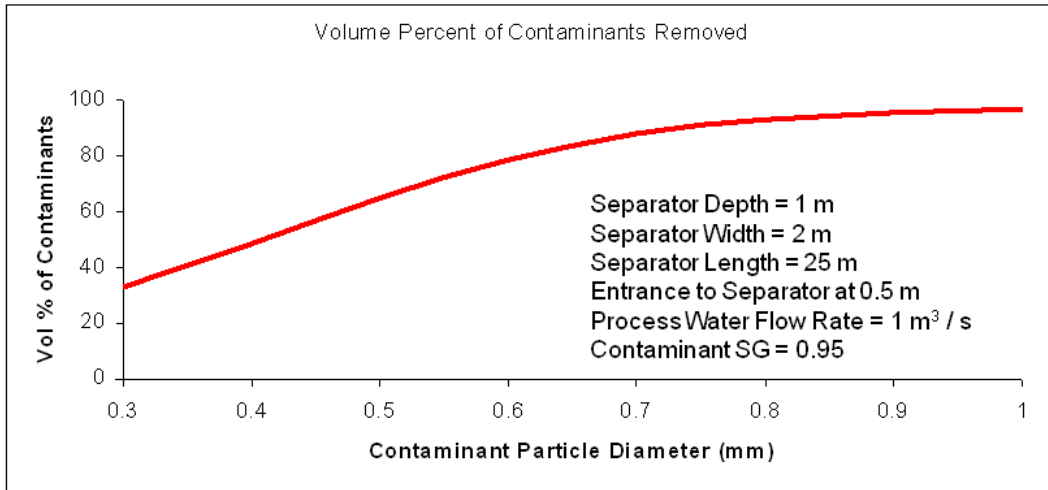
Peters, M., Timmerhaus, K., & West, R. (2002). *Plant Design and Economics for Chemical Engineers, 5th Edition*. McGraw-Hill.

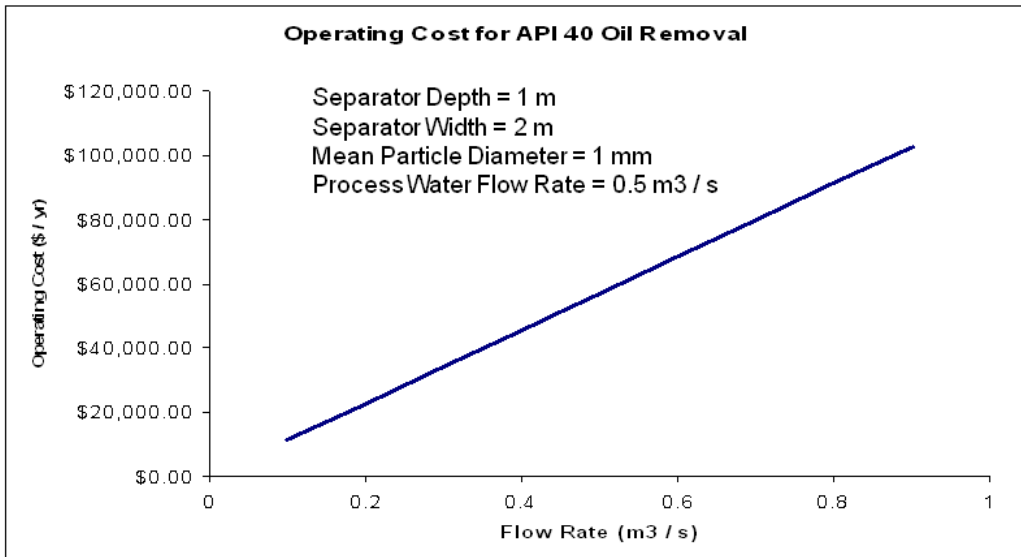
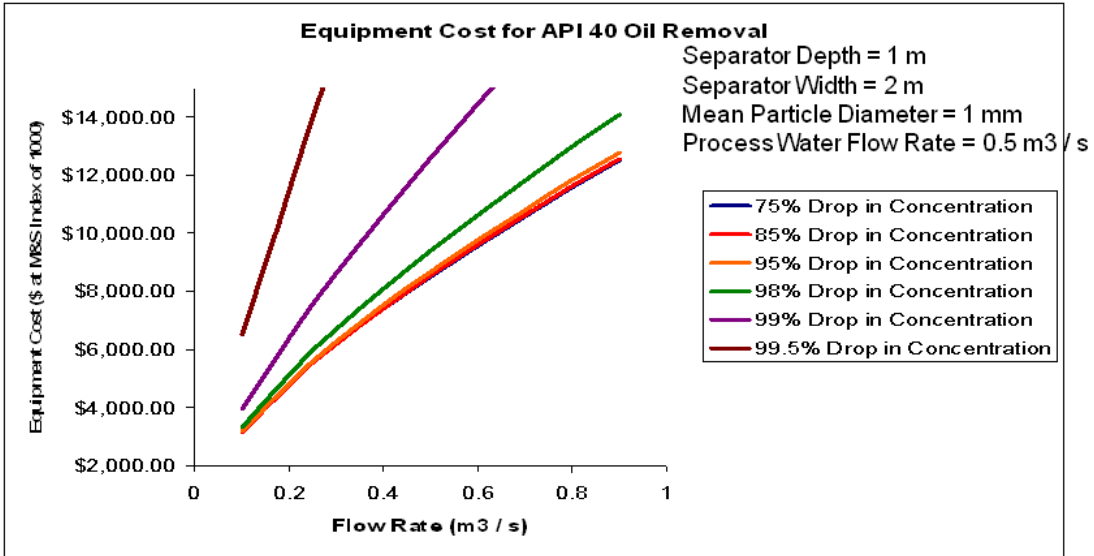
# Appendices

## API Separation

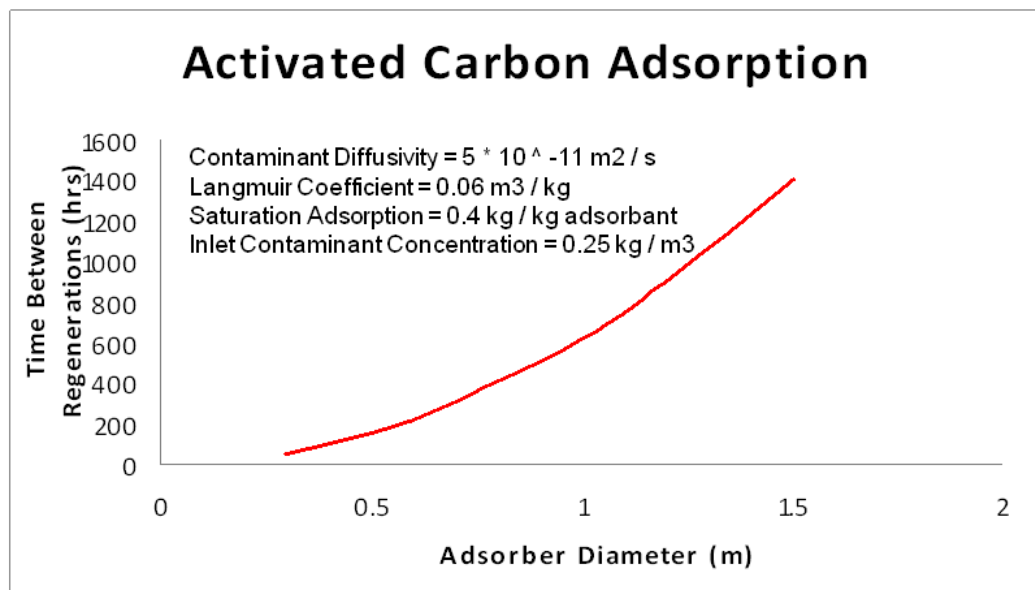
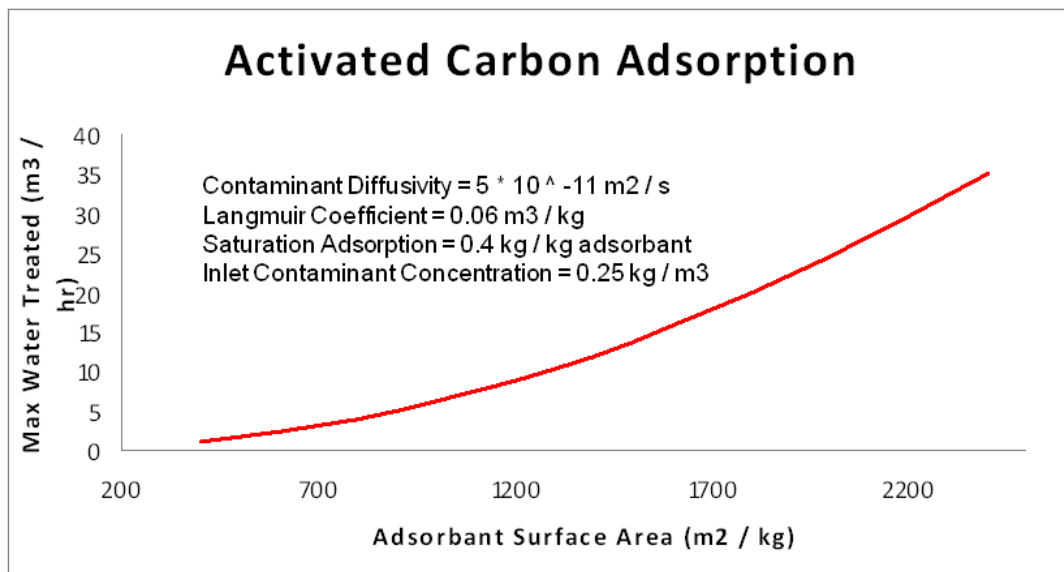




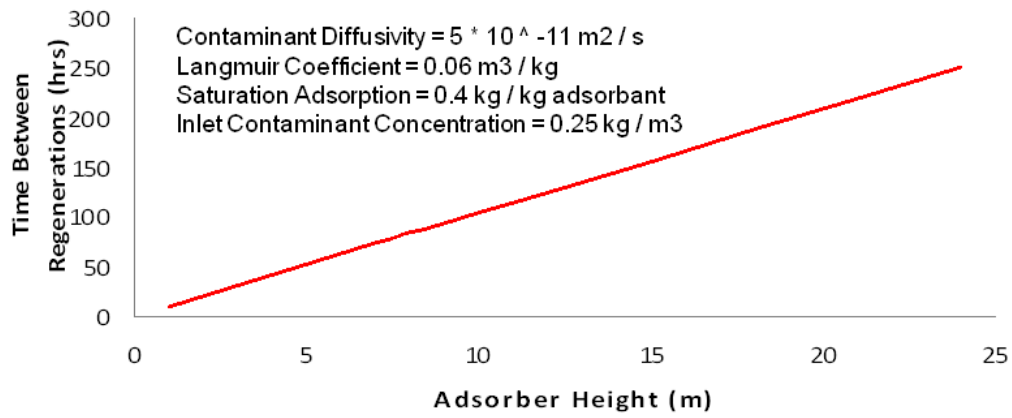




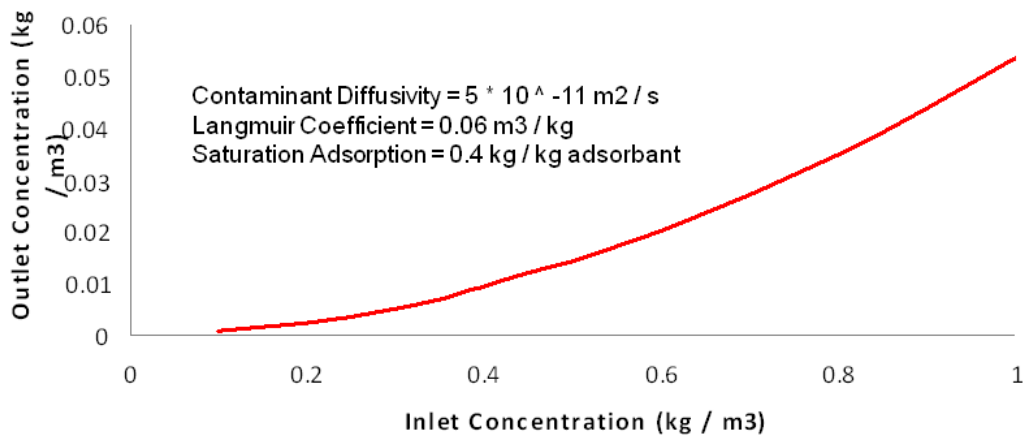
## Activated Carbon Adsorption



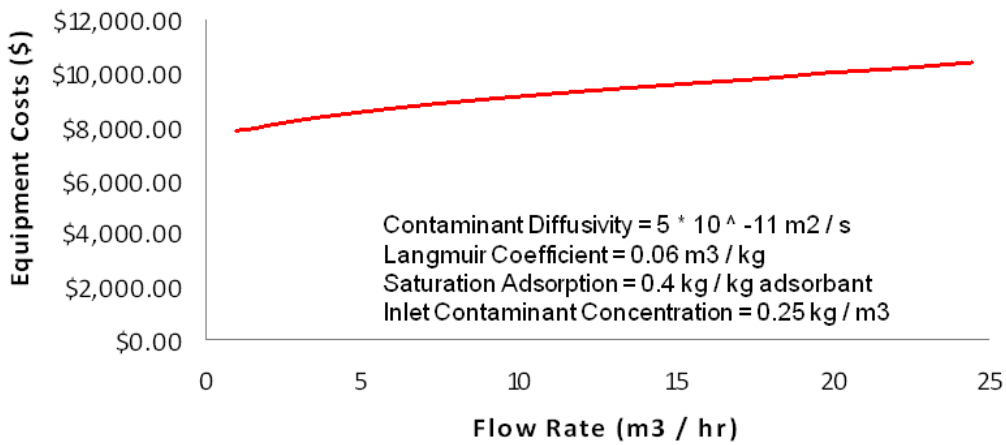
## Activated Carbon Adsorption



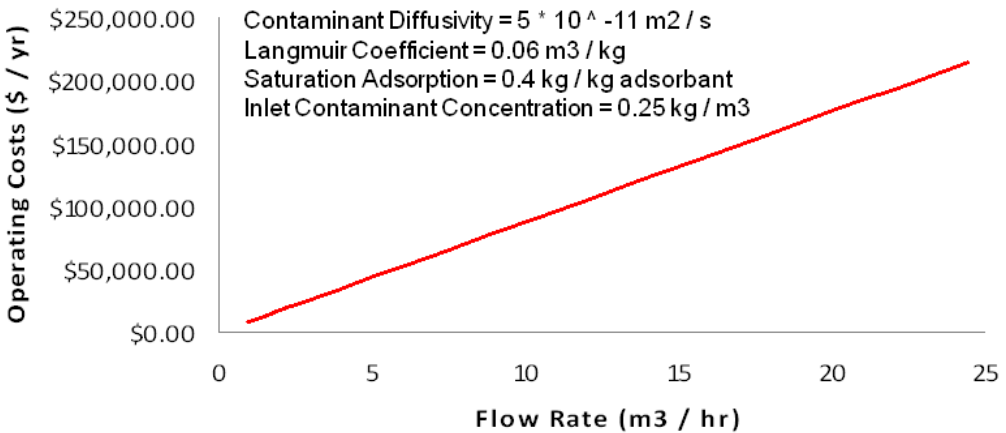
## Activated Carbon Adsorption



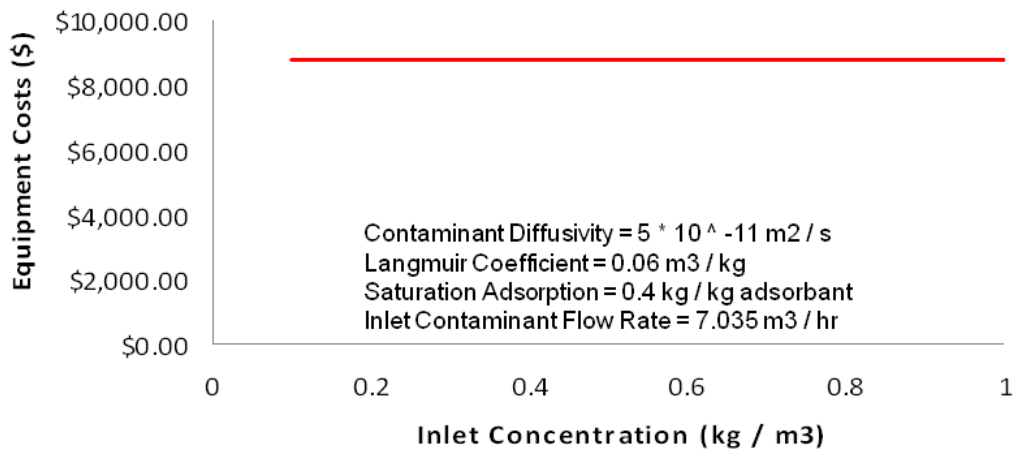
## Activated Carbon Adsorption



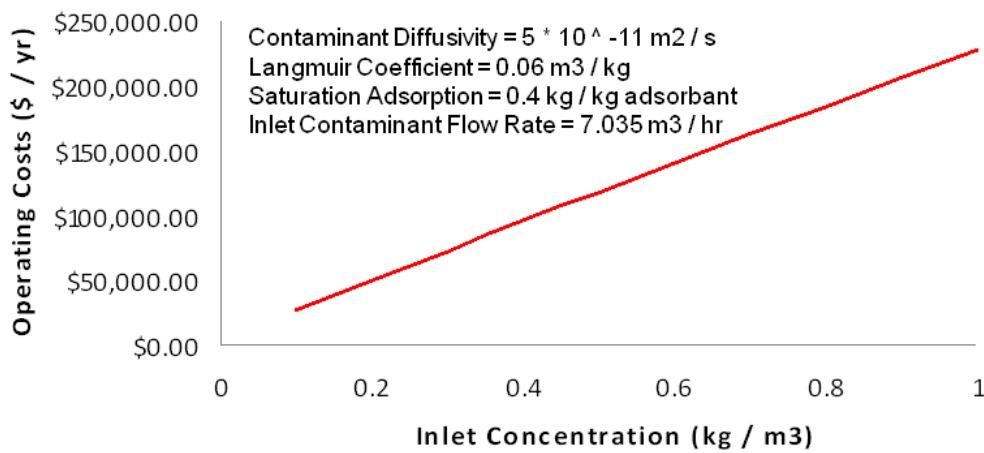
## Activated Carbon Adsorption



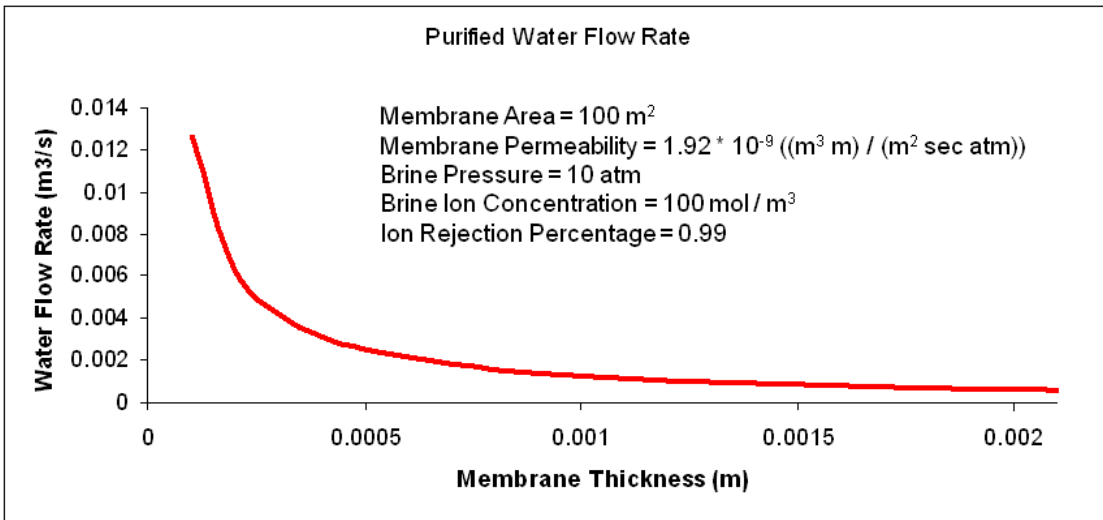
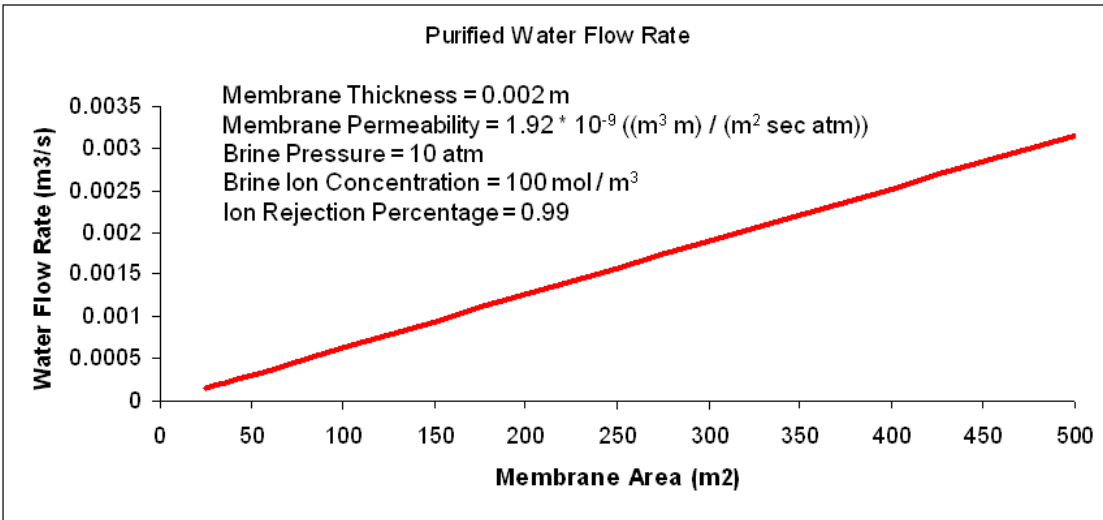
## Activated Carbon Adsorption

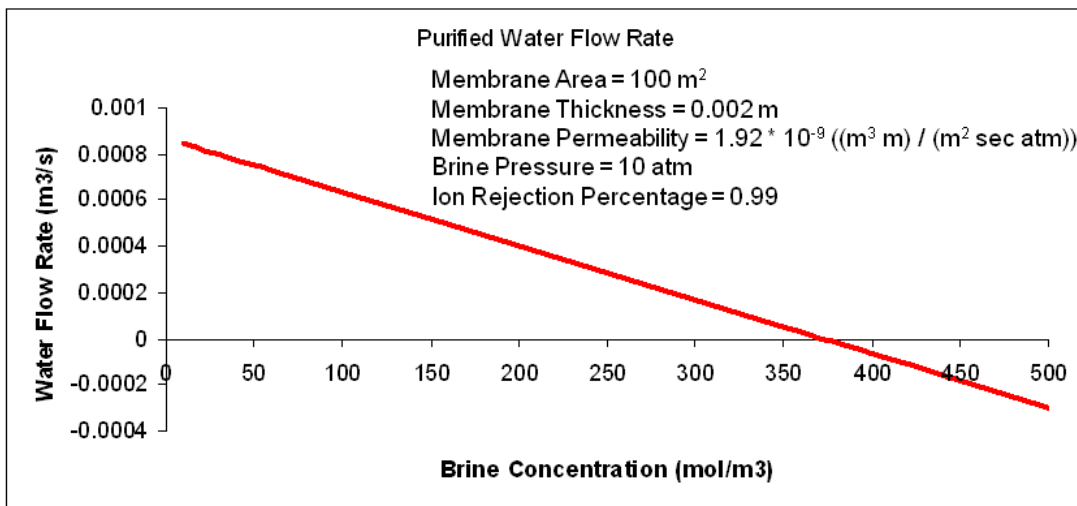
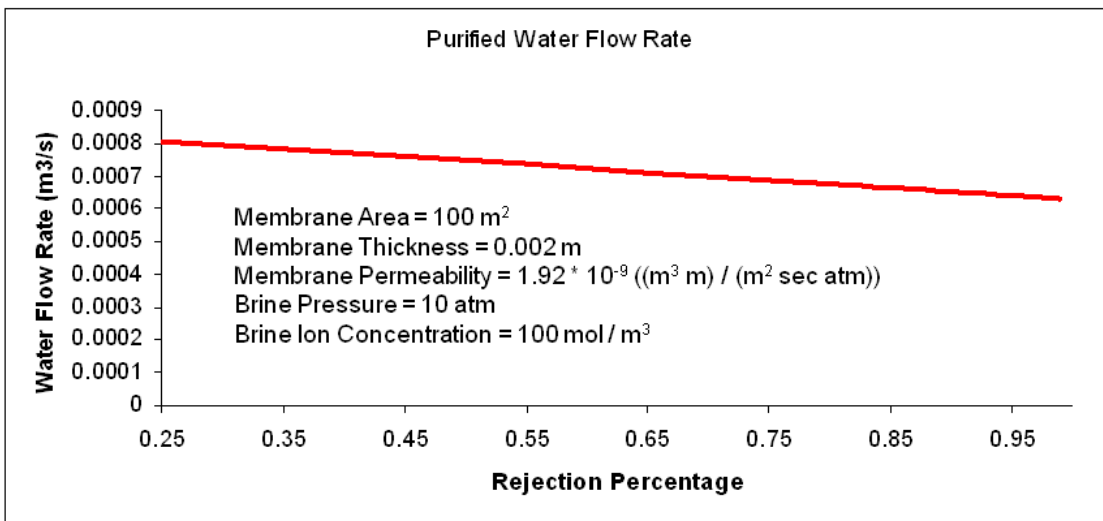
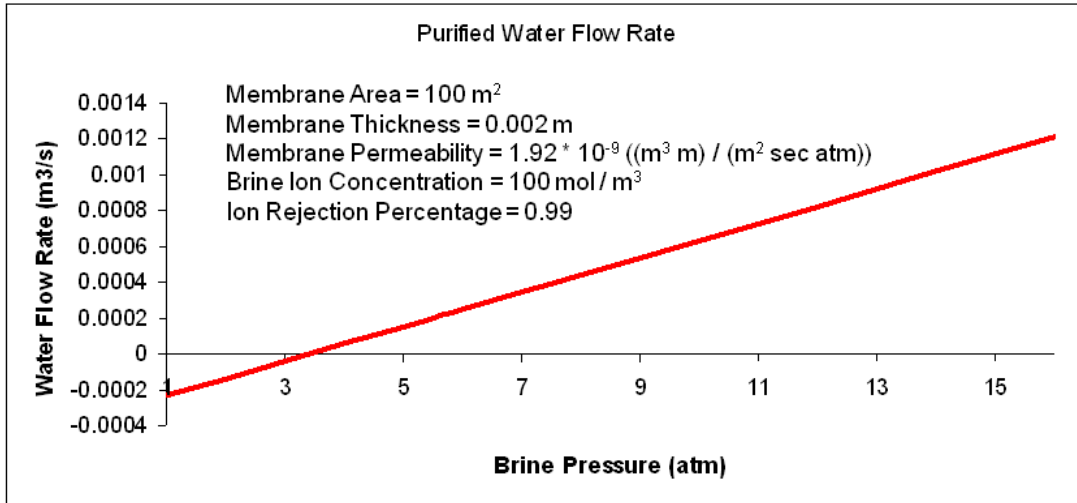


## Activated Carbon Adsorption

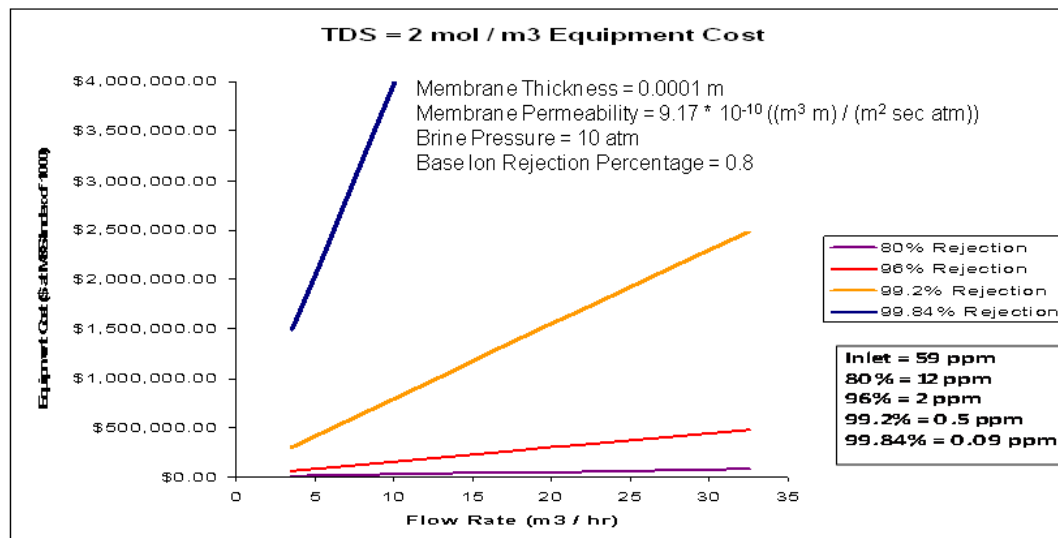
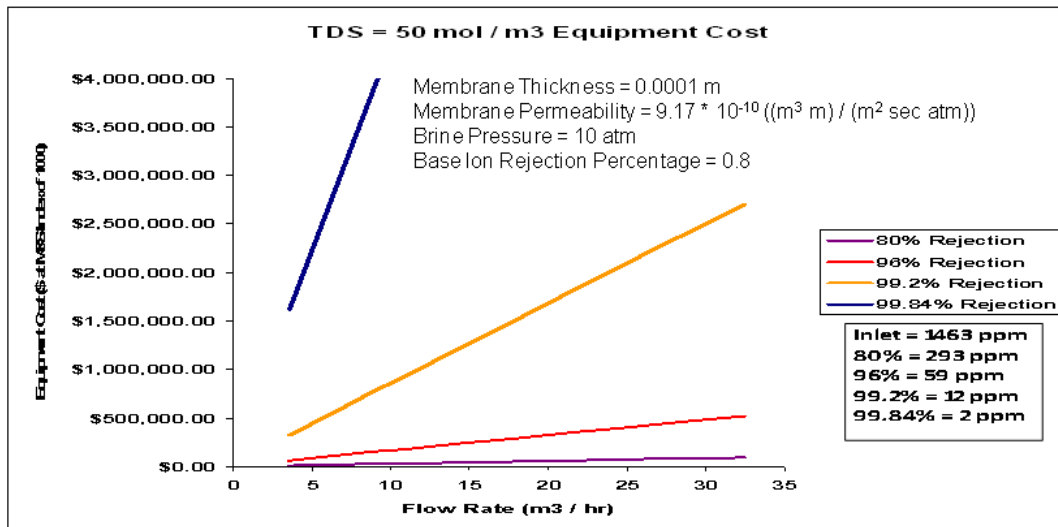
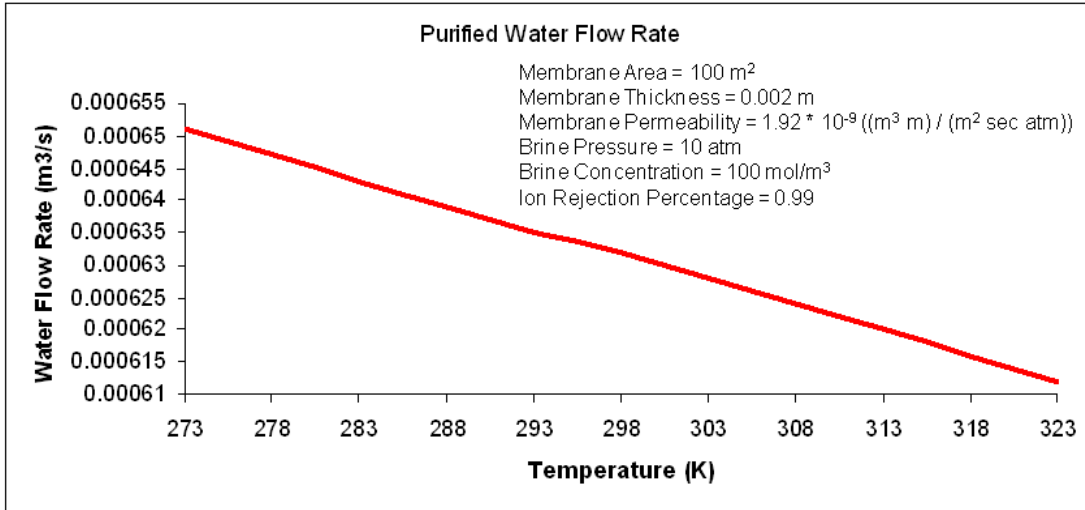


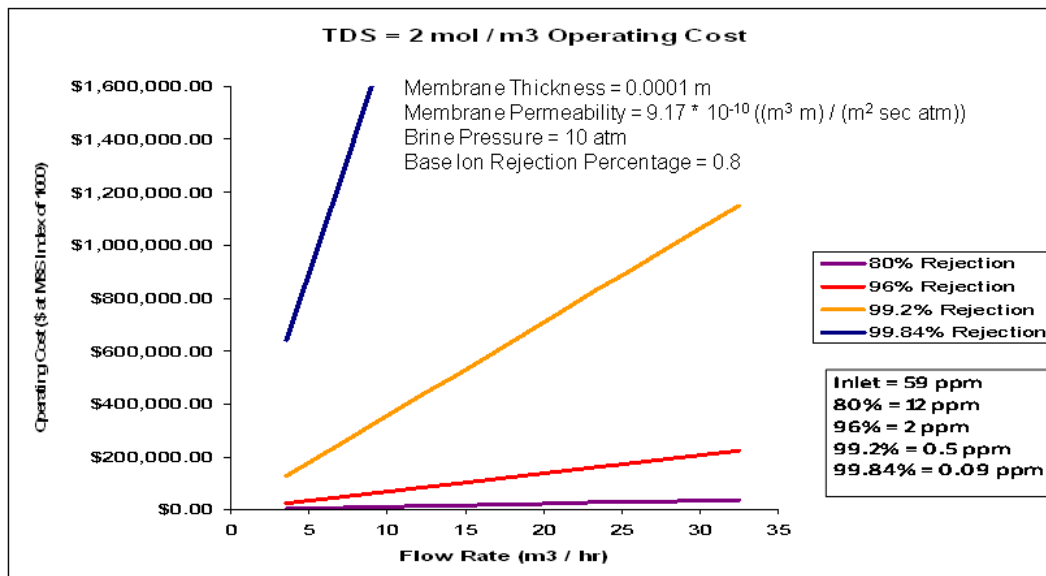
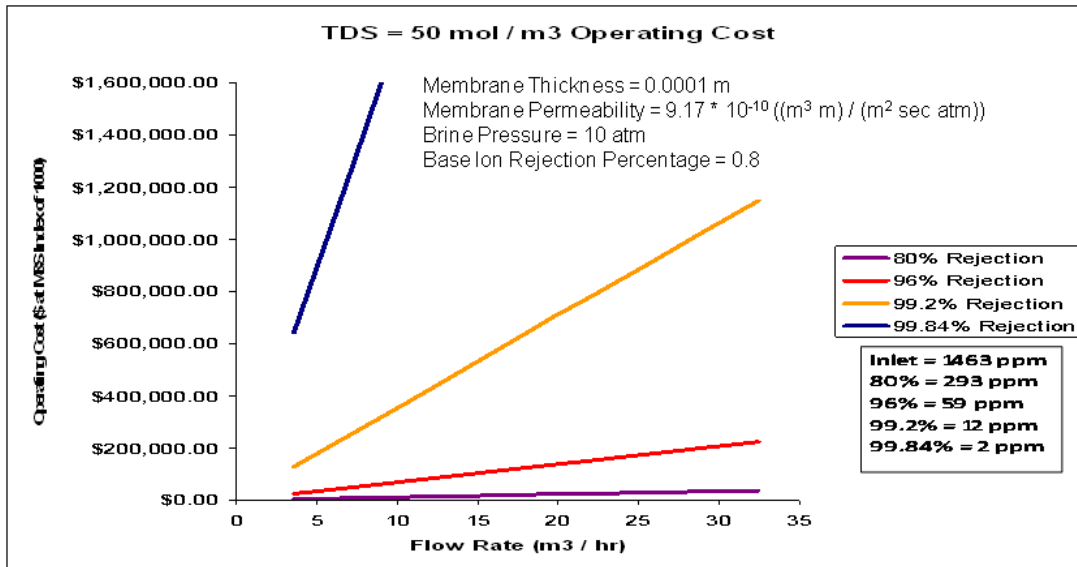
# Reverse Osmosis











# Chevron Wastewater Treatment

